# IRRADIATION OF ETHYLENIC COMPOUNDS

# WITH GAMMA-RAYS.

by

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# INTRODUCTION.

Radiation chemistry, the study of the chemical effects induced by ionising radiation from radioactive elements or from other short-wave radiation sources, is at present in a state of rapid development. Although it dates from 1896, when Becquerel noted that radiations from pitchblende could fog a photographic plate, some fifty years were to pass before radiation research was to become possible on a large scale. This was due, primarily, to the fact that early workers utilised the radiations produced by naturally occurring radioactive isotopes and it was not until after the Second World War, when the importance of plutonium-239 as a nuclear explosive led to its production in quantity, that radioactive materials became readily available.

Since 1945, therefore, radioactive isotopes, either as waste by-products from atomic piles or produced for specific purposes, have found a greatly increased field of application in chemical, medical and industrial research. For example, if the Fe-55 content of oil used in an engine whose piston ring has been irradiated with neutrons is determined, the wear on the piston ring can be accurately assessed. Metallic castings may be radiographed for defects and flaws of all kinds by the use of a cobalt-60 gamma ray source and suitable photographic plates. Iodine-131 is used extensively in medical research, as are cobalt and tantalum for radiotherapy.

Another reason for the time lag in the development of radiation research was the obvious health hazard encountered by the workers in this field. However, the dangers of high intensity sources and the necessary precautions are now well known and appreciated and there is little danger if these are rigorously observed.

Radiation chemistry is a field closely related to photochemistry, although the energies involved are initially much larger, and many new problems are introduced, the latter, as it is normally studied, following a simpler pattern. The relatively low concentration of excited species in gas phase photochemistry ensures that one studies only the reaction of these with normal molecules, whereas in liquid phase radiation chemistry the number, nature and spatial distribution of the excited species are not known with any certainty.

There are two main approaches to the experimental study of radiation chemistry. The first involves the use of scavengers such as iodine[1] or diphenylpicrylhydrazyl[2] (D.P.P.H.) to trap the free radicals initially produced and thus obtain a direct measure of the radiation effects. If the numbers and also the nature of the initial excited species may be determined in this way, the subsequent reactions should be predictable. Magat and his co-workers[3] used D.P.P.H. for studies on the radiolysis of benzene and chloroform, but its use has been critised due to its own instability to high energy radiation. This is a common problem

in radiation chemistry as no substance appears to be completely inert to powerful ionising radiations and the solvents accepted for use in conventional chemistry may become important sources of other excited species. The second approach, that used in this present research, is to determine qualitatively and quantitatively the ultimate products and infer from them the nature of the primary interactions.

Various types of ionising radiation are used, alpha-, beta-, gamma-, or X-rays. However, only the interaction of gamma-rays with matter will be discussed, as the radiation source used in the present work was the cobalt isotope - cobalt-60. This isotope emits gamma-rays of energy 1.12 and 1.33 MeV, and beta-rays of 0.31 MeV[4]. As the latter are weak and their power of penetration is very small, their possible contribution has been ignored.

Although gamma-rays are similar to ultra-violet or visible light, but of much shorter wavelength, the energy of gamma-rays is almost entirely absorbed by the ejection of electrons from the atoms in an irradiated system. This may be accomplished by three processes[5-7], namely, the photoelectric effect, the Compton effect, and the pair formation effect.

The most important process at low energy, below 0.2 MeV, is the photoelectric effect. The energy in this case is utilised to eject a bound electron from a molecule with an energy equal to

the difference between the original quantum and the binding energy of the electron. This effect is more important for elements of higher atomic number, for example, it plays a more important role in the gamma-ray absorption of alkyl iodides than of alkyl chlorides.

At somewhat higher energies, the photoelectric effect becomes insignificant and a quantum, instead of giving up its entire energy, may transfer only part of its energy to the electron, being deflected from its original path, and allowing the process to be repeated. This is the Compton scattering or recoil effect.

The pair formation effect, involving the formation of a positron-electron pair, cannot occur until the energy of the photon is greater than 1.02 MeV, and is not important until much higher energies are involved.

Excited molecules may be produced in two ways,

a) by the direct interaction of the primary radiation or of secondary electrons with molecules in their paths,

b) by recombination of positive ions with electrons.

In either case, the excited molecule may then dissociate into free radicals but the latter process leads to more energetic radicals. In addition to this, the positive ions themselves may react with neutral molecules or undergo fission (as in the mass spectrometer). In fact, most of the chemical effects observed result from the formation of free radicals which may combine with one another or react with other molecules.

Modern work,[8,9] however, has tended to show the importance of ionic mechanisms, especially in the gas phase[10-12] where the ejected electron may escape more easily from the field of the newly formed positive ion.

The Radiolysis of Aqueous Solutions.

Due to the interest in biological effects of radiation, aqueous solutions have been a frequent subject for study in radiation chemistry, and although the work to be presented in this thesis is concerned with non-aqueous media, it will be of interest to note the major effects in this field.

Pure water produces H, OH, and $HO_2$ radicals together with molecular hydrogen and hydrogen peroxide[13], and the products from the irradiation of dilute aqueous solutions of organic compounds arise from the attack of these radicals on the organic molecule; for example, phenol is formed from the irradiation of benzene under those conditions[14]. Hydroxylation of many aliphatic and aromatic compounds has been shown, by Kailan[15], to be predominant in the radiolysis of aqueous systems. Irradiation of dilute aqueous solutions of nitrobenzene[16,17], chlorobenzene[18], and benzoic acid[19,20] shows that hydroxyl groups are introduced into the nucleus of the monosubstituted benzene independent of the nature of the group already present. This suggests free radical attack rather than

the usual ionic attack on the benzene nucleus.

The presence of oxygen may play a large part in the irradiation of aqueous solutions of organic compounds. Results from the irradiation of lactic acid[21], some B-hydroxy acids[22], and ethanol[23] have shown that the presence of oxygen greatly enhances the predominant reaction of oxidation ($RCH_2OH \rightarrow RCHO$). This, however, may not be attributed solely to the increased presence of hydroperoxide radicals ($H^{\cdot} + O_2 \rightarrow HO_2^{\cdot}$) or of molecular hydrogen peroxide, but also to the formation of peroxy radicals of type $RO_2$ produced by the addition of oxygen to an organic free radical. This oxidation suggested possible applications to carbohydrate chemistry; the irradiation of D-Glucose[24] produces D-Glucuronic acid, although the major product is glyoxal.

Another important effect noted in aqueous solution is the possibility of polymerisation. Acrylamide[25,26] and Acrylonitrile[27] have been polymerised in aqueous solutions and it was found that the rate of polymerisation is proportional to the square root of the dose rate. A post-irradiation effect was also noted.

A large volume of work is also being pursued in the irradiation of proteins, steriods, amino acids,and vitamins, etc., in aqueous solution, parallel to the investigation by radiobiologists of animal survival and radiation damage to specific organs.

The Radiolysis of Organic Compounds.

The study of the irradiation of organic compounds in the liquid phase may be conveniently divided into two main classes - the irradiation of pure compounds and the irradiation of compounds in solution.

The structure and nature of the compound to be irradiated influences greatly the type of reaction favoured in the irradiation of pure compounds. The product yields and number of products may vary greatly, dependent upon whether the compound in question is saturated or unsaturated.

The irradiation of hydrocarbons gives a large number of products in more or less comparable yields as well as numerous minor products. Such a result may be expected since it has been found that the initial splitting of hydrocarbons occurs at relatively random points in the carbon skeleton,[28,29] although Dewhurst has recently found in his study of the radiolysis of n-hexane that the ratio of C-C breaks to C-H breaks was greater than if this were completely true[30]. However, this is found with many compounds. Hummel, in the radiolysis of liquid methyl acetate with gamma radiation, found six gaseous and seventeen liquid products and stated that all bonds in the methyl acetate molecule appeared to be broken except the carbonyl double bond.[31]

The effect of radiation on alkyl halides, however, is more specific, as the predominant primary effect of the radiation

is to break the carbon-halogen bond[28,32]. There is effectively a single major reaction involved in the irradiation, for example, of butyl bromides[33] accompanied by a number of minor side reactions. It seems unlikely that this is due to preferential absorption of energy at the C-Br bond, since this cannot be explained, except to the extent that the local electron density is higher in that part of the molecule. A mechanism must exist, therefore, for the transfer of energy from other parts of the irradiated molecule to this bond.

Radiation induced reactions of unsaturated compounds have always been a popular field of study, due to the high product yields which may be of practical significance. Polymer formation is the predominant process in the irradiation of the alkenes, and the polymerisation of many types of monomers, acrylates, methacrylates, styrene, acrylonitrile, and vinyl compounds[34-37], has been studied in great detail. In most cases, the reactions proceed by means of a free radical induced chain reaction and therefore lead to very high yields. Recently, however, studies have been made of radiation induced reactions of unsaturated compounds which are not dependent on free radical initiation. Davison, Pinner and Worral have shown that the polymerisation of isobutene must proceed by an ionic mechanism[9] and it has also been claimed by Chang, Yang and Wagner that the direct dimerisation of some terminal olefins must be due to an ion-molecule mechanism[38].

The study of the irradiation of dilute solutions introduces

the concept of 'indirect action'. Due to the non-specificity of absorption, the chemical effects on the solute are more likely to result from attack by the primary products from the solvent rather than from a direct effect of the radiation on the solute.

An example of this latter type is the work of Miller, Stafford and Taylor[39] on solutions of benzene, toluene, and a number of aliphatic hydrocarbons in carbon tetrachloride which probably involves the attack of trichloromethyl radicals and chlorine atoms on the solutes. Feng and Mamula have studied benzene-carbon tetrafluoride mixtures and found that the major products were fluorobenzene and benzotrifluoride, although they suggest that the reaction is not free radical in nature[8]. The radiation induced chlorination and bromination of aromatic compounds are, however, typical free radical reactions[40,41].

The Present Approach.

When the present work was commenced, Miller, Stafford and Taylor had been studying the irradiation of both unsaturated and saturated compounds in this department and it was decided that this work should be restricted to the irradiation of other unsaturated aliphatic compounds.

Taylor had irradiated both cis- and trans-1, 2-dichloroethylene and the first part of this work was concerned with further studies on this system. The major part of the work was, however, concerned with the irradiation of allyl systems, mainly allyl bromide and allyl chloride, to determine the extent of the contribution made to the polymerisation by the breaking of the carbon-halogen bond.

Techniques.

The radiation unit used in this work was similar in design to that described by Gibson and Pearce[42] and had been set up in conjunction with A.E.R.E. Harwell in 1954.

In July, 1957 two cobalt-60 sources were installed; a 140 Curie vertically positioned source and a 64 Curie horizontal source. The sources were in the form of $^{60}Co$ pellets mounted in aluminium tubes which could be withdrawn electrically into a concrete block, or put into the radiation chamber as required.

Most irradiations, for which no rigorous precautions were taken to exclude air, were carried out in annular Pyrex glass vessels of capacity 50mls to 2000 mls, fitted with Quickfit stoppers. However, for more accurate quantitative work, Pyrex glass tubes of 80ml capacity were used. It was possible to irradiate eight of these tubes at the same time by placing them in fixed positions in a metal ring attached to the source tube with the source at the centre. It was confirmed experimentally that the same amount of radiation was received by each of the tubes placed in this way.

All radiation vessels used were previously treated with chromic acid, thoroughly rinsed with distilled water and dried in an electric oven.

Dosimetry.

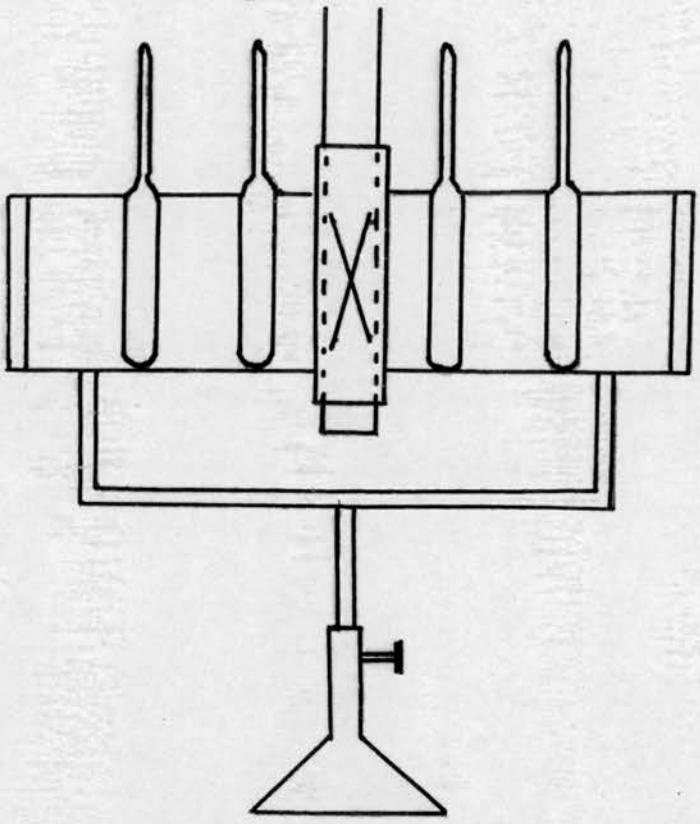
It is necessary to measure the energy absorbed in a solution exposed to radiation for quantitative results to be obtained.

The units normally used in this work, to measure the energy absorption or dose are the roentgen (r) or the electron volt (eV). The roentgen is conveniently defined as the radiation unit from which one ml. of water absorbs 93 ergs of energy. (One eV is equivalent to $1.60 \times 10^{-12}$ ergs). The rate of energy absorption, or dose rate, can therefore be expressed in roentgens or electron volts, per unit time per unit volume of absorbing medium,

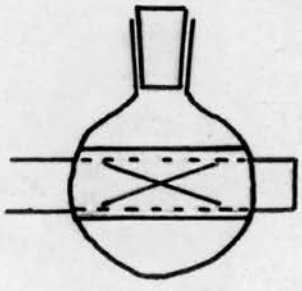
FIGURE I

IRRADIATION VESSELS

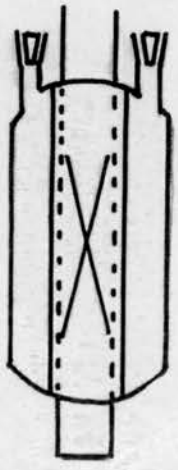
METAL RING WITH TUBES



ANNULAR VESSELS



HORIZONTAL SOURCE



VERTICAL SOURCE

for example, r/ml/min.

The accurate measurement of absorbed energy by irradiated materials has been a protracted problem and it has become standard practice to use, for dose-rate determination, a radiation induced chemical reaction whose dose-rate dependence has been studied. For such measurements, the reaction involved must be independent of dose rate over a wide range and relatively insensitive to the presence of impurities. Probably the most satisfactory reaction is the oxidation of ferrous sulphate in aerated 0.5 to 1$\bar{N}$ aqueous sulphuric acid[43,44]. The chemical yield and energy input of this reaction have been measured accurately by various methods[45,47] whose results are in good agreement for a value of 15.5 ± 0.2 ferric ions produced per 100 electron volts absorbed in the system[44]. This value is referred to as the 'G value' for the oxidation of ferrous ions. Yields of products from the irradiation of chemical compounds are usually given in this way. The G value refers to the number of molecules produced or decomposed for each 100 electron volts of energy absorbed and is normally indicated thus:-

$G_{(-Fe^{++})} = 15.5 \pm 0.2$ or $G_{(Fe^{+++})} = 15.5 \pm 0.2$.

Some physical changes, notably the colouration of certain glasses[48] or rigid polyvinyl films[49], have also been considered as dosimeters as well as innumerable chemical reactions[20,50-53], but the 'Fricke' or ferrous sulphate dosimeter has been shown to be very reliable in most cases. However, for total doses of less than 2000r, it is not sensitive enough and for doses greater than

50,000r air saturated solutions become depleted of oxygen, if in a closed system, and the ferric yield falls[43].

As has already been mentioned, absorption of the energy of $^{60}Co$ gamma radiation takes place predominantly by Compton scattering. The energy absorption by any given material, therefore, is proportional to its electron concentration and, consequently, a correction must be made for this when comparing the energy absorbed by a system with that absorbed by the ferrous sulphate solution under otherwise identical conditions.

The energy absorbed per unit volume (E ergs/$cm^3$) is related to the flux of radiation (I ergs/$cm^3$) by the relation

$E = Iu$ where u is the absorption coefficient of the material

$u = Ne_e\sigma_a$ where Ne is the number of electrons per unit volume and $_e\sigma_a$ is the electronic absorption cross-section for Compton scattering. As this latter function is a constant for radiation of a given frequency and the geometry of the two systems is identical, the ratio of the electron densities gives the ratio of the energy absorption by the two systems. Therefore,

$$\text{energy absorbed by organic solution} = \text{energy absorbed by ferrous solution} \times \frac{\text{Ne organic}}{\text{Ne ferrous}}$$

where the electron density (Ne) of 1 ml of liquid is given by

$$Ne = \frac{d}{M} \times N \times A$$

where d = density of the liquid

M = Molecular weight of the liquid.

N = Avogadro's number

A = sum of the atomic numbers of the different atoms in the molecule.

The electron density of the ferrous solution is obtained by treating it as pure water with a density of 1.023 $gm/cm^3$.

Experimental Determination of Dose Rate.

The reagents required for the ferrous sulphate dosimeter were

1) Analar Ferrous Ammonium Sulphate.
2) Analar Sulphuric Acid.
3) Pure water - free from organic impurities.

The water was prepared by subjecting tap water to a three stage distillation process i.e., the water was distilled from an acid potassium dichromate solution, then from potassium carbonate solution and finally redistilled without reagent present. The distillation apparatus was made of Pyrex glass and the water was stored in a silica glass vessel. All glass apparatus used in dosimetry was thoroughly cleaned in chromic acid, distilled water and finally 'triple-distilled' water before use.

Solutions of $\frac{M}{100}$ ferrous ammonium sulphate 0.8 $\bar{N}$ with respect to sulphuric acid were prepared with the pure water. The irradiation vessel for which the dose-rate was required was filled with this solution and placed in position in the radiation

chamber. Samples were then removed at intervals and the ferric ion concentration was measured spectrophotometrically with a Unicam SP500 by comparing the transmission of the irradiated sample with that of the original solution at 304mμ. The molar extinction coefficient of the ferric ion in 0.8 N sulphuric acid at this wavelength is accurately known (Table 1) and the concentration was calculated from the equation

$$\log \frac{I_o}{I} = ecd$$

where e = molar extinction coefficient

c = concentration in moles per litre

d = cell thickness (cms)

From the concentrations of ferric ions found, it was possible to find the rate of production of ferric ions per minute and, using the value of $G_{(Fe^{+++})} = 15.5$, the dose-rate $(E)_{Fe^{++}}$ was calculated.

Supposing X molecules of organic product were formed per ml per minute from the irradiation of the same vessel occupying the same position on the source, then the G. value for the production of the organic product is given by

$$(G\ org) = \frac{100\ X}{(E\ org)}$$

where $(E\ org) = E_{(Fe^{++})} \times \frac{Ne\ org}{Ne_{(Fe^{++})}}$ eV/ml/min.

The irradiation vessels used in this work received dose-rates of 400 to 2000 r/ml/min.

Table 1.

The molar extinction coefficient for ferric ions in 0.8 $\bar{N}$ sulphuric acid solution at 304 mμ.

| $T^{o}C$ | e |
|---|---|
| 15 | 2074 |
| 16 | 2089 |
| 17 | 2104 |
| 18 | 2119 |
| 19 | 2135 |
| 20 | 2150 |
| 21 | 2165 |
| 22 | 2181 |
| 23 | 2197 |
| 24 | 2213 |
| 25 | 2229 |

e: molar extinction coefficient at a temperature of $T^{o}C$.

Gas Liquid Chromatography.

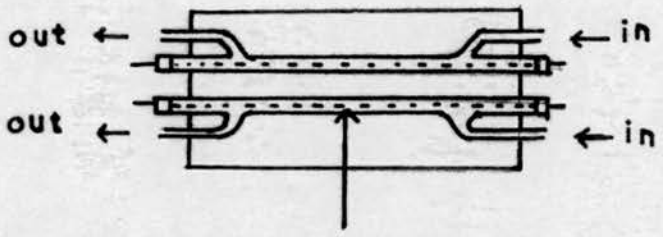
The low G values of many reactions had necessitated the use of some highly sensitive analytical technique at the outset of radiation chemistry in this department. Miller and Taylor had therefore constructed several gas-liquid chromatography units of conventional design, and since the technique has now become commonplace[54-57], only a cursory description of the analytical G.L.C. used will be given.

The detectors in use when this work started were iron alloy thermocouples supported in protecting silica glass capillaries above small hydrogen flames. Although this type of detector was very useful for normal qualitative work, it became extremely sensitive to external disturbances when run at high sensitivity. The sensitivity of these detectors was also very dependent on the nature of the compounds concerned. Accurate quantitative estimates could be obtained only by injecting samples of prepared standards until a duplication of the peaks produced by the unknown mixture was achieved.

Accordingly, all the detection units were later converted to the katharometer type. An example is shown in Figure 2. The katharometer was in the form of a metal block, suitably drilled, with two stretched tungsten filaments placed in the gas streams through the block. The filaments formed two arms of a Wheatstone bridge network, Figure 2, current to the bridge being supplied by

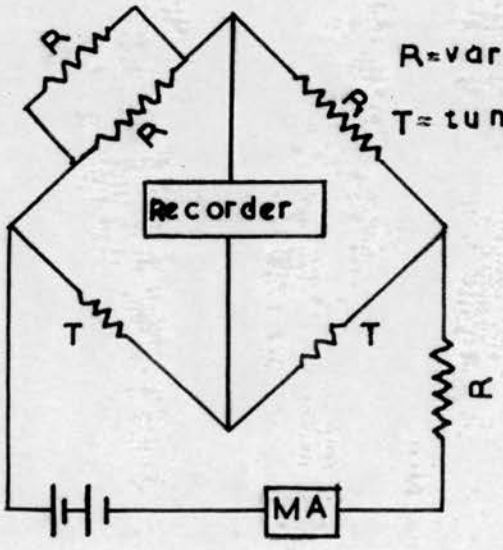
FIGURE 2

KATHAROMETER BLOCK




TUNGSTEN FILAMENT

KATHAROMETER ELECTRICAL CIRCUIT




R=variable resistance

T= tungsten filament

2-volt accumulators. The out of balance e.m.f. was measured on a 500 microvolt, full scale deflection Sunvic recorder. The sensitivity of the detector was controlled by altering the bridge current by means of a variable resistance in series with the accumulators.

This type of detector was used initially in a conventional low temperature apparatus and was kept at room temperature, being well lagged as a protection against sudden external changes in temperature. Later, however, it was adapted for use at high temperature. This was accomplished by placing the lagged unit in a glass beaker wound with resistance tape which was supplied with current from a Variac transformer whose input voltage was stabilised. The heater was insulated by mounting it in another lagged beaker which was placed in a box packed with asbestos waste. As the katharometer itself was insulated from the heater, it required a few hours to come to equilibrium after any change was made in the voltage supplied to the heater. However, when equilibrium had been attained, the temperature of the detector block was constant to $\pm$ 0.5° at 100°C.

The chromatographic columns were Pyrex glass tubes of 5 mm internal diameter and 45 to 150 cm total length. They were kept at steady temperatures inside thermally insulated heaters made from glass tubing as already described. Adequate temperature control was obtained in this way ($\pm$ 1° at 100°C). In the high

temperature units, it was important to ensure that the injection point, the exit tubes between the column heater and the detection unit, as well as the katharometer itself, were maintained at a temperature above the boiling point of the injected sample. Each unit required a buffered flow of oxygen-free nitrogen or hydrogen from the cylinders and this was achieved by means of a reducing valve, a needle valve, and a number of glass buffer vessels placed in series. A portion of the gas was allowed to escape through vertical columns of water which acted as safety valves and pressure regulators.

Various column packings were employed; the most frequently used stationary liquid phases were B.D.H. tricresyl phosphate, silicone elastomer (E 301, Griffin and George) and silicone fluid (MS 550, Hopkin and Williams). The tricresyl phosphate (T.C.P.) gave extremely good separations for most of the halogenated compounds used in this work, and was the most favoured stationary phase, but could not be employed above 160°C because of its tendency to volatilise from the column packing (column stripping). At higher temperatures, therefore, the silicone fluid and elastomer were used. These oils (20% - 30% by weight) were absorbed on Johns-Manville celite (60-90 mesh) or crushed firebrick which had been elutriated with water to remove dust, dried and graded.

During the period of this work, a Griffin and George Mark IIa gas phase chromatographic unit was acquired. This was

of conventional design, employing katharometer detectors and a reduced outlet pressure, and need not be described further.

Preparative Gas Liquid Chromatography.

In addition to the analytical apparatus already described, a large scale G.L.C. unit was constructed. This was capable of separating 2-3 mls of mixtures, whereas in the analytical apparatus, only about 0.01 - 0.05 ml was injected.

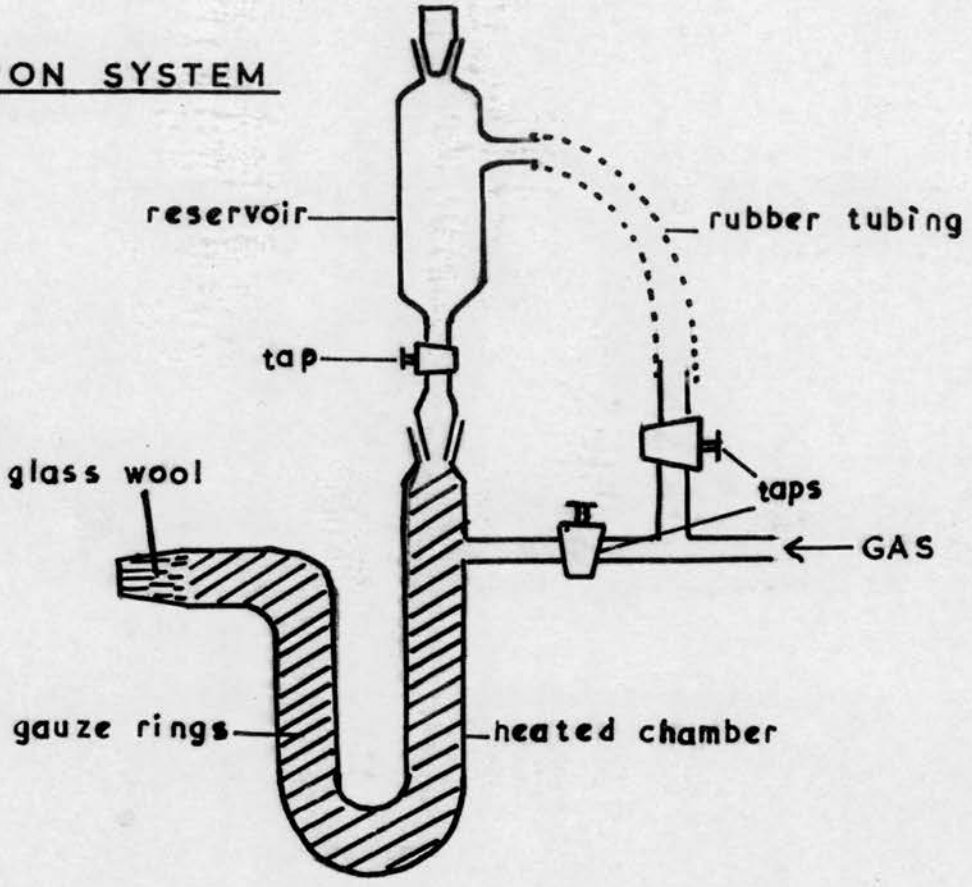
The unit consisted, initially, of two 8' columns (25 mm.i.d.) mounted in electrically heated jackets which could be used singly or joined up giving a 16' length of column. The injection system was able to vaporise a large sample and is shown in Figure 3. By manipulation of the taps, the sample was delivered rapidly from the reservoir into an electrically heated vapourising chamber filled with Dixon stainless steel gauze rings or glass helices.

The detector used was a katharometer of the same type as used for the analytical columns. Early experiments, however, had indicated that this was both unstable and insensitive. Both these defects were found to be due to the high gas flow rates used, (200 - 400 ml/min), and were overcome by the introduction of a bypass system which only allowed a small fraction of the gas emerging from the column to pass over the filament. The reference filament of the detector was sealed off and used merely as a fixed resistance. The rest of the electrical system was the same as shown in Figure 2. A similar problem, due to high

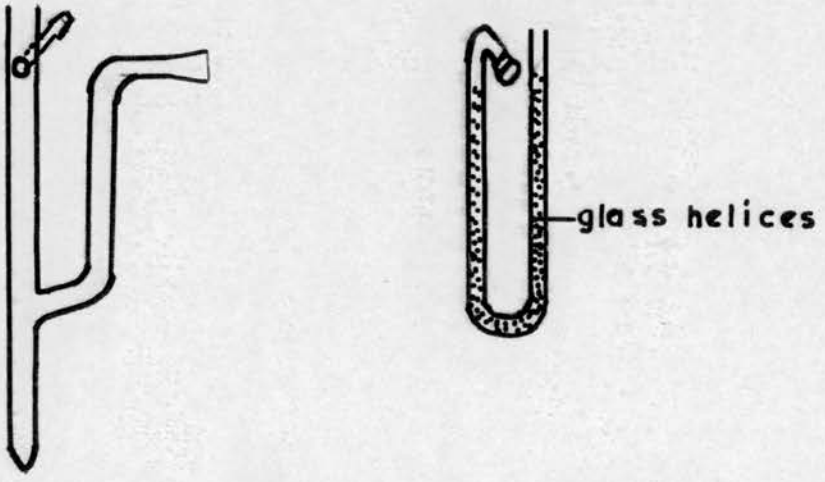
FIGURE 3

PREPARATIVE SCALE G.L.C.

INJECTION SYSTEM




TRAPS



gas flow rate has since been reported by Atkinson and Tuey[58].

Recovery of the separated components of an injection was the most serious problem encountered, due to the presence of a large proportion of non-condensable gas. Numerous patterns of trap have been reported and some workers have advocated the use of adsorbents such as alumina[59]. In the present work, the latter course was not adopted as the aim was to produce a purified sample in a directly usable form. The major loss of material was due to fog formation and in an endeavour to precipitate the fog, the traps were filled with glass beads or helices and cooled in liquid nitrogen. However, due to the amount of material involved, the trap became blocked by deposition of solid. The traps finally used consisted of two U-shaped parts (Figure 3). The first section, which had a well at the bottom, was empty and was connected to the other part, which was filled with glass helices. Most of the vapour condensed in the first part, the liquid running into the well, and the remaining fog passed on to the second part, where further condensation occurred. The amount of liquid condensed in the helix packed half was rarely able to cause blockage and an overall recovery of about 80 - 90% was obtained. After the sample had been collected, it was possible to distil the liquid from the second part into the main trap by heating the former electrically, passing a slow stream of nitrogen through it and again cooling the main trap in liquid nitrogen. The well at the bottom of this trap could then be removed by

cutting the glass tube and the sample obtained for investigation.

It was soon realised that the very long columns were unnecessary except for the most difficult separations. Large gas flows and high temperatures were necessary in order to minimise retention times and, under these conditions, column stripping became a very troublesome problem. It was found impossible to use T.C.P. above 130° or silicone elastomer above 180°. Shorter lengths of column, however, proved to be equally successful for most separations, provided that the internal diameter of the column was also reduced (3' column length of 20 mm. i.d., 2' column length of 15 mm. i.d.) It was then found possible to operate at much lower temperatures, well below the boiling points of the injected compounds, provided the injection system was efficient and the outlet tubes and detector were maintained at a temperature high enough to prevent condensation. Extremely satisfactory separations were achieved under these conditions for most mixtures; apparently, the lower temperature increased the separation factor more than the loss incurred by shortening the column length.

## SECTION I

### The Irradiation of the Allyl Halides:

### Allyl Chloride, Allyl Bromide, and Allyl Iodide.

The radiation chemistry of allyl compounds has not been so extensively investigated as that of vinyl compounds. This is mainly because the latter class of compounds were known to polymerise with great ease under normal conditions using peroxide catalysts and it was soon realised that such results might also be expected from the irradiation of these compounds as previously described. Allyl compounds, however, only polymerise with difficulty to give products of low molecular weight under catalytic conditions.

One of the earliest observations of polymeric material from the allyl halides was made by Staudinger and Fleitmann[60] who illuminated allyl chloride with ultra-violet light and, after eight days, noted 30% conversion to a very viscous liquid polymer. By study of the reduced product from the photopolymerisation, it was concluded that its structure was essentially as shown below

$$n\ CH_2 = CH - CH_2Cl \longrightarrow \left[ - CH_2 - \underset{\displaystyle CH_2Cl}{\overset{\displaystyle |}{CH}} - \right]_n$$

where n = 5 to 25, average about 10.

Polymers of moderate size have also been made with catalysts. Bartlett and Altschul[61] found one polyallyl chloride, from exhaustive polymerisation using benzoyl peroxide, which had an average of 6.3 allyl chloride units per molecule. Such polymerisations using benzoyl peroxide have been conducted by heating under reflux[62] or at higher temperatures in a pressure vessel[63]. A polymer, of about 4 units per molecule, was made by treating allyl chloride with boron trifluoride in the presence

of Raney nickel at low temperature[64].

A more recent study of the benzoyl peroxide catalysed polymerisation of allyl chloride has been made by Frank and Blackham[81] who found that below 100°C only liquid polymer was formed but that at higher temperatures a dimer of unknown structure could be detected. The ratio of dimer to total polymer increases with temperature, at 130° the ratio was 0.19 and at 165°C it was 0.32.

Similar liquid polymer yields for allyl bromide and allyl iodide were also noted by Staudinger and Fleitmann[60]. Kharasch and Buchi[65] studied the decomposition of diacetyl peroxide in allyl bromide and found that a dimer of allyl bromide was formed in good yield. This was shown to be 5-bromo-4-bromomethyl-pent-1-ene.

A number of studies[66-68] of allyl polymerisations have also been made in an attempt to explain the formation of only low molecular weight polymers and will be discussed later. A comprehensive review of allyl polymerisations has also appeared[69].

Preparation of pure allyl bromide.

B.D.H. allyl bromide was purified by distillation, using a 3' Fenske ring packed fractionation column which had a mirrored vacuum jacket, to prevent heat loss, along its entire length. The rate of take-off of the distillate was regulated by an adjustable take-off head and the distillate was monitored by G.L.C. using a 3' column of 30% T.C.P. on firebrick (60-90 mesh) at 80°C. Initially, the allyl bromide was approximately 98% pure, the impurities being of lower b.p., and distillation was continued until the distillate contained approximately 0.1% impurity. The allyl bromide remaining in the still pot was then given a quick distillation to free it from any higher boiling material. The allyl bromide used in the large irradiations contained not more than 0.05% impurity, $n_D^{20}$ 1.4660 (Literature $n_D^{20}$ 1.4654)

Care was also taken to ensure that the allyl bromide was dry, as it was known that water was sometimes used as a stabilising agent for allyl halides[70]. The allyl bromide was therefore allowed to stand overnight with anhydrous sodium sulphate or calcium chloride before distillation.

Irradiation of allyl bromide.

435 mls of the purified dry allyl bromide were irradiated in a stoppered annular Pyrex glass vessel at a dose rate of approximately 1300r/ml/min for 336 hours.

A direct injection of the irradiated solution into the

G.L.C. apparatus, using a 3' column of 30% T.C.P. on firebrick (60-90 mesh) at 80°C showed the presence of a number of products which were more volatile than the allyl bromide, one being eluted in approximately thirty seconds, which meant that its boiling point was well below 0°C. An injection was also made at a higher temperature (160°C) which showed the presence, initially, of some six higher boiling products whose boiling points ranged from 100° to 200°C. One peak, however, was much larger than any of the others; this later proved to be the dimer of allyl bromide. Attempts were made to determine free bromine or hydrogen bromide in the irradiated solution but none was found.

The allyl bromide and more volatile products were, therefore, distilled off and the very volatile product was collected in a trap, cooled in liquid nitrogen, attached to the receiving flask. This product was identified as pure propylene by G.L.C., using a column packing of 30% octyl phthalate on alumina. The distillate collected in the receiving flask was retained for further investigation of the more volatile products

When the allyl bromide had been removed, the residue (85 gms) was distilled at 15 mm pressure, again using a liquid nitrogen cooled trap attached to the receiving flask. Most of the residue boiled at 93-95°C at 15 mm pressure, but by G.L.C., it was shown that this compound was still impure (~5% total impurity). Further attempts to purify this compound by distillation and freezing methods have proved to be only of limited value.

This distillate was readily identified as the dimer of allyl bromide, $n_D^{20}$ 1.5260 (Lit. $n_D^{20}$ 1.5256; b.p. = 93-95°C/15 mm). Kharasch and Buchi[65] had isolated this compound from the decomposition of diacetyl peroxide in allyl bromide and proved that its structure is 5-bromo-4-bromomethyl-pent-1-ene.

A chemical analysis of this compound was obtained

| Analysis found | Analysis calculated for $C_6H_{10}Br_2$ |
|---|---|
| C = 29.29% | C = 29.8% |
| H = 3.89% | H = 4.14% |
| Br= 66.8% | Br= 66.19% |
| Total 99.98 | Molecular weight = 242 |

The molecular weight was determined, by the elevation of the boiling point of pure benzene, and was found to be 241. An infra-red spectrum of this compound was also obtained which showed the presence of vinyl type unsaturation with absorptions at 1643, 995, and 920 $cm^{-1}$ (The infra-red spectra are given at the end of this section, p. 48 ).

On treating a solution of this irradiation product dissolved in carbon tetrachloride (5 gms in 20 ml $CCl_4$) with a solution of bromine in carbon tetrachloride, the bromine was rapidly decolourised. The addition of bromine was continued until the yellow colour did not fade. The carbon tetrachloride was then removed and the residue, 1,2,5-tribromo-4-bromomethyl-pentane, distilled at 120-130°C at 0.05 mm press. $n_D^{20}$ 1.5907 (Lit. $n_D^{20}$ 1.5909).

A chemical analysis of this compound gave the following result

| Analysis found | Analysis calculated for $C_6H_{10}Br_4$ |
|---|---|
| C = 17.98% | C = 17.91% |
| H = 2.52% | H = 2.49% |
| Br= 79.78% | Br= 79.6% |
| Total 100.28 | |

The identification of the allyl bromide dimer was completed by reacting 10 gms of it dissolved in benzene with N-sodiophenylhydrazine which had been prepared by adding 16 gms of phenylhydrazine to a benzene suspension of 6 gms of sodamide[71]. This reaction mixture was heated under reflux for 10 hours during which time a large quantity of sodium bromide was precipitated. The reaction mixture was then poured into water and the product was extracted with ether, the ether extract being washed repeatedly with water to remove phenylhydrazine. The product was then extracted from the ether with 2N HCl, the acid solution was made alkaline and the product extracted again with ether and dried. After removal of the ether, the residue, 1-phenyl-4-allyl-pyrazolidine, was distilled, b.p. = 135°C/0.05 mm (Lit. b.p. = 130°C/0.01 mm) The picrolonate of this compound was then prepared and gave yellow needles from ethanol, m.p. 185°C, (Lit. m.p. 186-187°C.)

The cold trap fraction, 1.5 ml, obtained during the

distillation of the dimer was found to contain three radiation products whose boiling points ranged from approximately 140° to 160°C and which could not be separated by further distillation. At least two of these compounds were known to be unsaturated as they disappeared on bromination of a sample of irradiated allyl bromide, the third G.L.C. peak was merely reduced. These compounds could, however, be separated by preparative scale G.L.C. using a 3' column (i.d. 20 mm) containing 30% tricresyl phosphate on very fine graded firebrick (>90 mesh) at 98°C with a flow rate of 300 mls/min of nitrogen. The first fraction was eluted in 40 minutes, the second after 100 minutes, and the third after 130 minutes.

A chemical analysis of fraction 2, which was a powerful lachrymator, suggested an empirical formula of $C_3H_4Br_2$

| Analysis found. | Analysis calculated for $C_3H_4Br_2$ |
|---|---|
| C = 20.86% | C = 18% |
| H = 2.38% | H = 2% |
| Br= 76.60% | Br= 80% |
| Total 99.84 | |

This analysis, although poor, was considered good enough, as the sample was not redistilled after collection and may have been contaminated with a small amount of the G.L.C. stationary phase. An infra-red spectrum of this compound showed absorptions at 1616cm$^{-1}$ and 1308cm$^{-1}$ and no absorptions at 930-950cm$^{-1}$. (See spectrum on p.49 ) This suggested the presence of a cis

disubstituted ethylenic double bond and on comparing this spectrum with one obtained from cis-1, 3-dibromo-prop-1-ene, they were found to be identical. The latter compound had been prepared by the action of phosphorus oxychloride on 1, 3-dibromohydrin which gave a mixture of the cis and trans isomers of 1, 3-dibromo-prop-1-ene[72]. The two isomers, whose physical constants and infra-red spectra have been discussed by Harwell and Hatch,[80] were separated by preparative scale G.L.C. using the column described for the separation of the radiation products.

The refractive indices of the radiation product and the synthesised compound gave further confirmation that the former was cis-1, 3-dibromo-prop-1-ene.

Radiation product $n_D^{20}$ 1.5538 Synthesised compound $n_D^{20}$ 1.5540 (Lit. $n_D^{20}$ 1.5550)

A chemical analysis of fraction 3 also suggested an empirical formula of $C_3H_4Br_2$ or $C_3H_6Br_2$

| Analysis found. | Analysis calc. for $C_3H_4Br_2$ | Analysis calc. $C_3H_6Br_2$ |
|---|---|---|
| C = 18.89% | C = 18% | C = 17.82% |
| H = 2.79% | H = 2% | H = 2.97% |
| Br= 78.30% | Br= 80% | Br= 79.2% |
| Total 99.98 | | |

This fraction, which was also lachrymatory, was known to contain a saturated compound, believed to be 1,3-dibromopropane, from bromination studies used in conjunction with G.L.C.

However, on examining its infra-red spectrum, unsaturation, due to the presence of a trans disubstituted double bond, was indicated by strong absorptions at 1617cm$^{-1}$, 1239cm$^{-1}$ and 934cm$^{-1}$. On comparing this spectrum with those of a number of pure unsaturated compounds, whose presence was believed possible from G.L.C., no close similarity could be detected. When the spectrum of the radiation product was compared, however, with those of 1, 3-dibromopropane and pure trans-1, 3-dibromoprop-1-ene (p.46 ), it was soon realised that this fraction was a mixture of these two compounds. Attempts have since been made to separate these compounds by G.L.C. but even on very efficient analytical columns, this was found to be impossible.

The presence of 1, 3-dibromopropane in fraction 2 was confirmed by brominating a sample (0.5 gm) of the mixture dissolved in 1 ml of carbon tetrachloride. After the bromination was completed, the whole reaction mixture was injected into the preparative scale G.L.C. unit under suitable conditions. The, now, pure 1, 3-dibromopropane was trapped out and its infra-red spectrum was found to be identical with that of an authentic standard. The refractive index was also measured - $n_D^{20}$ = 1.5224 (Lit. $n_D^{20}$ 1.5233).

The first fraction which was eluted in the separation of the irradiation products by G.L.C. has proved to be very difficult to identify.

A chemical analysis was obtained -

| Analysis found. | Analysis calc. $C_3H_4Br_2$ | Analysis calc. $C_6H_9Br$ |
|---|---|---|
| C = 37.43% | C = 18% | C = 44.7% |
| H = 5.19% | H = 2% | H = 5.59% |
| Br= 56.90% | Br= 80% | Br= 49.49% |
| Total 99.52 | | |

This fraction, therefore, appeared to be neither a pure dibromo $C_3$ compound nor a monobromo $C_6$ compound, although its boiling point (approximately 130°-140°C) suggested these possibilities. A mixture of such compounds seemed possible. Attempts were made to show that this was a mixture by G.L.C., and by using a 3' column of 30% T.C.P. on firebrick (60-90 mesh) a partial separation into two components was noted at 100°C. The infra-red spectrum of this mixture was compared with those of 1-bromo-hexa-2,5-diene, and 3-bromo-hexa-1, 5-diene (which had been prepared by the action of N-bromosuccinimide on hexa-1, 5-diene (diallyl)[73], and separated by preparative scale G.L.C.) and with that of 1,2-dibromopropane but none of these compounds appeared to be present.

It may be possible, however, that one of the components of this fraction is formed by radiolysis of the allyl bromide dimer giving 4-bromomethyl-pent-1-ene as the infra-red spectrum of the mixture shows clearly the presence of a vinyl type double bond (3080,1643, 992 and 912$cm^{-1}$) a methyl group (1378$cm^{-1}$), and a $-CH_2Br$ group (2960, and 1437$cm^{-1}$). At present, no structure can be assigned to the dibromo $C_3$ component. It shows an

absorption at 960cm$^{-1}$ which suggests a trans disubstituted ethylenic double bond and would exclude the possibility of this compound being 3,3-dibromoprop-1-ene. 1,2-dibromoprop-1-ene is a possibility although its formation is considered to be unlikely.

In the initial injection of the irradiated allyl bromide at 160°C, two other products, which were in small yield, had been detected. One was eluted immediately before the dimer of allyl bromide and the other immediately behind the dimer. Careful distillation of the dimer mixture was unable to effect any significant concentration of these two compounds and, as they were in such small yield, (about 5% of dimer mixture) preparative scale G.L.C. was inapplicable. However, from bromination studies of the radiation mixture, it was discovered that the less volatile component was saturated and its G.L.C. characteristics resembled those of 1,2,3-tribromopropane. The dimer mixture (25 gm) was therefore brominated in carbon tetrachloride solution and, after the unsaturated compounds had been destroyed, the solvent was removed. Distillation of the residue gave a component (5 gm) boiling at 60°C at 0.5 mm pressure which on G.L.C. analysis was found to be still slightly impure. This compound was purified by preparative scale G.L.C. using an 18" column of 30% T.C.P. on firebrick at 130°C, and a chemical analysis was obtained which suggested an empirical formula of $C_3H_5Br_3$.

| Analysis found. | Analysis calculated for $C_3H_5Br_3$ |
|---|---|
| C = 14.48% | C = 12.8% |
| H = 2.25% | H = 1.8% |
| Br = 83.40% | Br = 85.4% |
| Total 100.13 | |

Once again, the analysis was poor, but as the preparative scale G.L.C. column was at 130°C, a small amount of contamination with T.C.P. is expected. An infra-red spectrum of this compound showed it to be identical with 1,2,3-tribromopropane.

$n_D^{20}$ 1.5840 (Lit. $n_D^{20}$ 1.5860)

After the distillation of the dimer mixture from the radiation products, a small amount of dark brown viscous oil remained. Further distillation at 0.5 mm pressure using a molecular distillation apparatus gave a number of small fractions. The first three fractions boiling at 50°, 60° and 70°C showed the appearance of another unknown compound contaminated with small amounts of dimer. Fractions were then obtained in which this compound was nearly pure and these were redistilled, giving a compound boiling at 90°C at 0.5 mm pressure.

A chemical analysis of this compound suggested an empirical formula of $C_6H_{11}Br_3$.

| Analysis found. | | Analysis calculated for $C_6H_{11}Br_3$ | |
|---|---|---|---|
| C | = 25.13% | C | = 22.19% |
| H | = 3.71% | H | = 3.41% |
| Br | = 71.2% | Br | = 74.3% |
| Total | 100.04% | | |

An infra-red spectrum of this compound confirmed that it was saturated and showed clearly the presence of a $C-CH_3$ grouping, from an absorption at 1385$cm^{-1}$, which suggested that this compound was 1,4-dibromo-2-bromo-methylpentane. Kharasch isolated a compound which he suggested was 1,5-dibromo-2-bromo methylpentane, whose refractive index was $n_D^{20}$ 1.5672[65]. The refractive index of the radiation product, however, was $n_D^{20}$ 1.5461 which compared well with that for 1,4-dibromo-2-bromo-methylpentane ($n_D^{20}$ 1.5454) which had also been prepared by Kharasch as a by-product of the reaction between 4-hydroxymethyl-pent-1-en-5-ol and phosphorus tribromide by which he had originally synthesised the allyl bromide dimer.

Hydrobromic acid, prepared by the addition of bromine to tetrahydronaphthalene[74], was therefore reacted with 5-bromo-4-bromomethyl-pent-1-ene, using aluminium bromide as a catalyst, in an attempt to synthesise the radiation product. Distillation of the reaction mixture after 10% conversion, gave a product (b.p. = 90-95°C/0.05mm., $n_D^{20}$ 1.5458) whose infra-red spectrum was identical to that of the radiation product. A chemical

analysis of this compound showed the presence of 73.9% Br and 22.37% C (Calculated for $C_6H_{11}Br_3$ - 74.3% Br, 22.19% C).

Distillation of the radiation products, after the removal of the 1,4-dibromo-2-bromomethyl-pentane, was continued, using a molecular cup still. 0.3 gms of a viscous distillate ($n_D^{20}$ 1.5540) was collected at 0.1 mm pressure with an oil bath temperature of 140°C. An infra-red spectrum of this compound showed the presence of unsaturation and a chemical analysis suggested an empirical formula of $C_3H_5Br$, i.e. that of allyl bromide itself.

| Analysis found | | Analysis calculated for $C_3H_5Br$. | |
|---|---|---|---|
| C = | 29.52% | C = | 29.8% |
| H = | 3.9% | H = | 4.14% |
| Br = | 66.7% | Br = | 66.8% |
| Total | 100.12 | | |

From this scant information, due to lack of material, it is suggested that this compound may be a trimer of allyl bromide.

The remaining black solid residue from the irradiation was washed with chloroform and dried in vacuo at 80°C. This solid, which was insoluble in all the solvents used, gave a bromine analysis of 26.4% and may be a decomposition product formed during distillation.

The only other product which has been isolated from the

irradiated allyl bromide is diallyl. This was first noted by G.L.C. and, by careful distillation of the allyl bromide, which was initially removed, a fraction enriched in this material was obtained. This was then injected into the 8' column of 30% T.C.P. on 40-60 firebrick at room temperature. The amount of this compound isolated was only sufficient for determination of its infra-red spectrum, which was identical with that of diallyl (1,5-hexadiene).

The yield of dimer was very much greater than that of any other irradiation product and further irradiations were carried out to determine the G value for its formation.

Determination of 100 eV yields for 5-bromo-4-bromomethyl-pent-1-ene.

The allyl bromide used in these irradiations was purified by subjecting the commercial product to the same distillation as already described and then to a further distillation using a 4' electrically heated fractionating column of Stedman stainless steel gauze rings (20 mm diameter) mounted in precision bore glass tubing (20 mm i.d.) which had a distillation efficiency of about fifty theoretical plates. The allyl bromide purified in this way showed no impurities on G.L.C. Care was taken that this allyl bromide was thoroughly dry as some samples used initially gave much reduced yields of dimer due to the presence of a small amount of water.

It had been intended to perform these irradiations

using degassed samples. However, because allyl bromide expands on solidifying, the normal degassing procedure could not be used. To remove most of the oxygen dissolved in the liquid, the allyl bromide was distilled under nitrogen immediately before use and after transferring the liquid to the irradiation tube, the tube was sealed off. The tubes used for these irradiations were Pyrex glass tubes of 80 ml capacity, which were irradiated on the inner ring of the metal stand, described in the introduction, at a dose-rate of $2.736 \times 10^{16}$ eV/ml/min, measured by the ferrous sulphate dosimeter.

The dimer formed in the irradiations was determined with an accuracy of 1% by G.L.C., using a 30% silicone elastomer on celite 545 (60-90 mesh) column at 150°C and 3 litres per hour flow rate. As the reproducibility of the injection size, on the commercial G.L.C. unit, was poor (~5%) an internal standard technique was used[75,76]. The internal marker used was o-dichlorobenzene which did not interfere with any of the other compounds in the mixture, and the ratio of dimer peak height to standard peak height was used as a measure of the concentration of the dimer. This method also reduced any defects caused by slight temperature variation or by small changes in the flow rate from run to run. The amounts of o-dichlorobenzene used were such that the peak height ratio was nearly unity.

In each determination, the standards used had been prepared by weighing out quantities of dimer (96% pure), diluting

them to 5 mls with chloroform and adding them to 1 ml of a solution of o-dichlorobenzene in chloroform (5-10% concentrations were used). 5 mls of the irradiated mixture were also added to 1 ml of the same internal standard solution. From a graph of the peak height ratio against concentration of the dimer, the amount formed in the irradiation could be determined.

The dose-rate absorbed by the allyl bromide was calculated thus

Dose-rate absorbed = Dose-rate measured on ferrous sulphate dosimeter x conversion factor.

$$\text{Conversion factor} = \frac{\text{Ne allyl bromide}}{\text{Ne ferrous sulphate}}$$

$$= \frac{1.398}{121} \times N \times 58 \div 5.682 \times 10^{-1}\ N.$$

$$= \frac{6.702 \times 10^{-1} \times N}{5.682 \times 10^{-1} \times N}$$

$$= 1.18$$

$$\text{Dose-rate absorbed} = (2.736 \times 1.18) \times 10^{16}\ \text{eV/ml/min.}$$

$$= 3.228 \times 10^{16}\ \text{eV/ml/min.}$$

The results are given in Table 2, and from the graph of the number of moles of product formed per ml of irradiated solution against total dose absorbed per ml (Fig. 4 ) the G value for the production of allyl bromide dimer was found to be 68.6.

Preparation of pure allyl chloride.

B.D.H. allyl chloride was dried and purified in the same

way as described for allyl bromide, $n_D^{20}$ 1.4160 (Lit. $n_D^{20}$ 1.4160). This allyl chloride contained approximately 0.1% of a less volatile impurity.

Irradiation of allyl chloride.

435 mls of the purified, dry allyl chloride were irradiated in a stoppered annular Pyrex glass vessel at a dose-rate of approximately 1300r/ml/min for 150 hours.

A direct G.L.C. injection of the allyl chloride failed to detect any volatile products formed during the irradiation. The unchanged allyl chloride was, therefore, removed by distillation and the residual product was 120 gms of a very viscous colourless oil. Distillation of this product, using a molecular still, was attempted without any success, although the oil became yellow in colour (O.B.T. 200°C).

A chemical analysis of this residual product gave the empirical formula $C_3H_5Cl$, which is that of allyl chloride itself.

| Analysis found | | Analysis calculated for $C_3H_5Cl$. | |
|---|---|---|---|
| C = | 47.22% | C = | 47.1% |
| H = | 5.88% | H = | 6.5% |
| Cl = | 46.3% | Cl = | 46.4% |
| Total | 99.4 | | |

The molecular weight of the product was found to be approximately 390 which suggested that the viscous oil is an

allyl chloride polymer of average degree of polymerisation equal to 5. An infra-red spectrum of the polymer showed the presence of unsaturation.

A series of irradiations were then made to determine quantitatively the amounts of polymer formed under the same experimental conditions that were used for the allyl bromide.

In these irradiations, the dose-rate was again $2.736 \times 10^{16}$ eV/ml/min, but the conversion factor was 0.863.

$$\text{Conversion factor} = \frac{\text{Ne allyl chloride}}{\text{Ne ferrous sulphate}}$$

where Ne allyl chloride $= \frac{p}{M} \times N \times Z = \frac{0.9382}{76.5} \times N \times 40$

$$= 4.905 \times 10^{-1} \times N$$

$$\text{Conversion factor} = \frac{4.905}{5.682}$$

$$= 0.863$$

The dose-rate absorbed by the allyl chloride was, therefore, $2.361 \times 10^{16}$ eV/ml/min.

The polyallyl chloride formed in these irradiations was determined by transferring the irradiated solution to a weighed flask, distilling off the unchanged monomer and weighing the residual polymer.

The results are listed in Table 3 and the G value for the production of polyallyl chloride, in molecules of monomer removed, was 369. This result was determined from a graph of the number of moles of monomer removed per ml against the total

dose absorbed per ml. (Fig. 5 )

Irradiation of allyl iodide.

B.D.H. allyl iodide was purified by fractional distillation until the initial impurities (abour 1%) were reduced to 0.1% in the remaining liquid. This liquid was then distilled under reduced pressure, b.p. 56°C/180 mm in darkness. This latter precaution was necessary as the allyl iodide was decomposed rapidly on exposure to light. The purified allyl iodide was pale yellow in colour, $n_D^{20}$ 1.5430 (Lit. $n_D^{20}$ 1.5437).

55 mls of the allyl iodide were irradiated in a stoppered annular Pyrex glass vessel at a dose-rate of approximately 2000r/ml/min for 160 hours.

Direct G.L.C. injections of the irradiated liquid, which was red in colour due to the presence of molecular iodine, failed to detect any significant quantity of volatile products except a small amount of a compound which appeared to be diallyl. After removal of unchanged allyl iodide, a small amount of dark tarry residue was left in the distillation flask.

No further irradiations of allyl iodide were carried out.

Table 2.

Dimer Yields from the Irradiation of Allyl Bromide.

| Volume Irradiated mls | Irradiation Time hours | Total dose absorbed eV/ml x $10^{-20}$ | Product (Dimer) gms/ml x $10^{2}$ | Product moles/ml x $10^{4}$ | G Value |
|---|---|---|---|---|---|
| 82.5 | 35 | .678 | 1.53 | .633 | 56.2 |
| 83 | 68 | 1.317 | 3.2 | 1.34 | 61.2 |
| 82 | 96 | 1.860 | 4.95 | 2.05 | 66.3 |
| 82 | 120 | 2.325 | 6.34 | 2.62 | 67.9 |
| 82 | 165 | 3.197 | 8.83 | 3.65 | 68.8 |
| 80 | 189 | 3.661 | 10.10 | 4.17 | 68.6 |
| 81 | 240 | 4.649 | 12.90 | 5.33 | 69.0 |
| 81 | 309 | 5.986 | 15.60 | 6.45 | 64.9 |

FIGURE 4

DIMER PRODUCTION FROM ALLYL BROMIDE

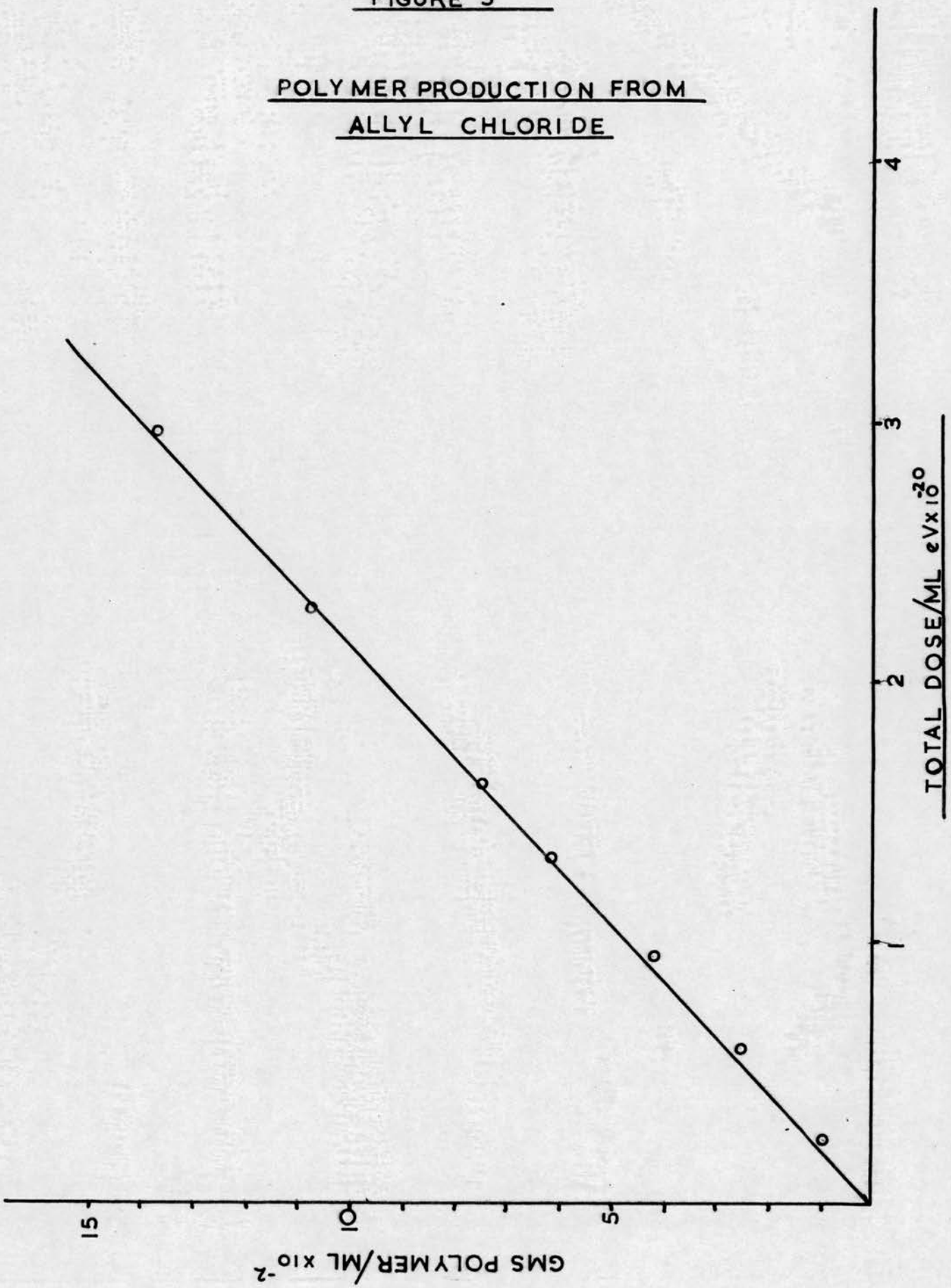
Table 3.

Polymer Yields from the Irradiation of Allyl Chloride.

| Volume Irradiated mls | Irradiation Time hours | Total dose absorbed eV/ml x $10^{-19}$ | Product Total Polymer gms | Product Total Polymer gms/ml x $10^{2}$ | Product Total Polymer Moles of $C_3H_5Cl$/mls $10^{4}$ | G Value |
|---|---|---|---|---|---|---|
| 82 | 18 | 2.55 | .7815 | .953 | 1.246 | 294 |
| 81.25 | 42 | 5.95 | 2.0613 | 2.536 | 3.315 | 336 |
| 81.75 | 67.5 | 9.56 | 3.4522 | 4.223 | 5.519 | 348 |
| 76.75 | 94 | 13.32 | 4.7516 | 6.191 | 8.092 | 366 |
| 79 | 114 | 16.15 | 5.9482 | 7.53 | 9.842 | 367 |
| 80.75 | 161 | 22.81 | 8.7027 | 10.80 | 14.12 | 373 |
| 77.5 | 209 | 29.61 | 10.5900 | 13.67 | 17.87 | 363 |

FIGURE 5

POLYMER PRODUCTION FROM ALLYL CHLORIDE



## Infra-Red Spectra.

All absorption frequencies are given in wave numbers ($cm^{-1}$), and the intensity of absorption is indicated by very strong (vs), strong (s), medium (m), or weak (w).

a) Product mixture from the irradiation of allyl bromide containing 1,3-dibromopropane and trans-1,3-dibromoprop-1-ene.

| Product Mixture | 1,3-dibromopropane | trans-1,3-dibromoprop-1-ene |
|---|---|---|
| 3065 w | | 3085 w |
| 2975 m | 2970 s | 2980 w |
| 2912 w | 2915 m | |
| 2850 w | 2850 w | |
| 1617 s | | 1621 s |
| 1432 s | 1432 vs | 1429 m |
| 1420 s | 1418 s | |
| 1348 w | 1350 m | |
| 1326 w | 1326 w | |
| 1293 s | 1292 vs | 1285 m |
| 1236 vs | 1236 vs | 1239 s |
| 1199 s | 1192 w | 1200 vs |
| | 1159 w | |
| 1121 w | 1120 w | 1120 w |
| 1071 w | 1071 m | |
| 1049 w | 1048 w | 1052 w |
| | 996 w | |
| 933 s | 939 s | 934 vs |
| 881 m | | 882 m |
| 850 m | 850 s | |
| 830 w | 830 m | |
| 759 s | 759 vs | |
| | | 727 w |
| 710 w | | 711 m |

b) Unidentified product mixture from the irradiation of allyl bromide, containing a dibromo $C_3$ component and a monobromo $C_6$ component. This table includes the spectra of 1,2-dibromo-propane and 1-bromo-hexa-2,5-diene and 3-bromo-hexa-1,5-diene.

| Product Mixture | 1,2-dibromo-propane | 1-bromo-hexa-2,5-diene | 3-bromo-hexa-1,5-diene |
|---|---|---|---|
| 3095 m | | 3090 w | 3090 m |
| | | 3020 w | 3020 w |
| 2980 s | 2975 s | 2985 w | 2970 m |
| 2940 s | 2925 s | 2900 w | 2920 w |
| 2885 m | 2860 m | | |
| 1837 w | | | 1850 w |
| 1644 s | | 1660 w | 1643 m |
| 1624 w | | 1648 m | |
| 1456 s | 1450 s | | |
| 1438 s | 1445 s | 1430 m | 1430 m |
| 1419 w | 1421 m | 1420 w | 1420 s |
| 1379 m | 1379 s | | |
| 1328 w | 1337 w | | |
| | 1313 m | | |
| 1286 w | | | |
| 1272 w | | | |
| | | | 1258 w |
| 1245 m | 1240 m | | 1230 w |
| 1228 m | 1225 m | | |
| | 1210 s | 1205 s | 1210 w |
| 1190 w | | | 1180 m |
| 1157 w | 1156 vs | | |
| | 1120 w | | |
| | 1095 w | | |
| | 1038 m | | 1042 w |
| | 1000 s | | |
| 992 s | | 990 m | 985 s |
| 962 m | | 965 s | |
| 912 vs | | 915 s | 920 vs |
| | 895 m | | |
| | 850 w | | |
| | 839 w | | |
| | 747 w | | 738 m |
| | | | 681 m |

c) Products from the irradiation of allyl bromide and from addition of bromine to 5-bromo-4-bromomethyl-pent-1-ene.

| 5-bromo-4-bromomethyl-pent-1-ene | 1,4-dibromo-2-bromomethyl-pentane | 1,2,5-tribromo-4-bromomethyl-pentane |
|---|---|---|
| 3080 w | | |
| | | 3010 m |
| 2970 m | 2980 m | 2980 m |
| | | 2965 w |
| 2920 w | 2935 w | |
| 2870 w | 2880 w | 2890 w |
| 1643 m | | |
| 1440 s | 1445 s | 1446 s |
| 1432 s | 1438 s | 1436 vs |
| | 1385 m | |
| 1350 w | 1346 w | 1342 w |
| | 1325 w | 1221 w |
| 1300 w | 1290 w | 1300 m |
| 1255 s | 1268 vs | 1263 vs |
| 1237 m | 1245 m | 1240 m |
| | 1225 w | |
| 1208 w | | |
| | 1171 w | 1150 m |
| | 1129 w | |
| | 1001 w | 1000 w |
| 995 m | | |
| | 972 w | |
| | | 953 w |
| 920 s | 920 w | |
| | | 891 w |
| 887 w | | 880 w |
| | | 857 w |
| 840 w | | |
| 835 w | 836 w | 835 w |

d) Products from the irradiation of allyl bromide.

| 1,5-hexadiene (diallyl) | | cis-1,3-dibromo-prop-1-ene | | 1,2,3-tribromo propane | |
|---|---|---|---|---|---|
| 3095 | s | 3080 | m | | |
| 3000 | s | 3033 | w | 3030 | w |
| | | 2966 | w | 2950 | w |
| 2935 | s | | | | |
| | | 2912 | w | | |
| 2865 | m | 2852 | w | | |
| 1833 | m | | | | |
| 1647 | s | 1650 | w | | |
| | | 1616 | vs | | |
| | | 1511 | w | | |
| 1445 | m | 1434 | s | 1429 | s |
| | | | | 1414 | vs |
| | | 1355 | w | | |
| | | 1347 | w | 1330 | m |
| | | 1308 | vs | | |
| | | | | 1252 | vs |
| | | | | 1231 | s |
| | | 1215 | s | 1212 | w |
| | | 1202 | vs | 1190 | vs |
| | | | | 1161 | m |
| | | 1123 | w | 1143 | w |
| | | | | 1111 | w |
| | | 1031 | w | | |
| | | 1012 | w | | |
| 992 | s | | | 998 | w |
| | | 966 | w | 956 | w |
| 910 | vs | 916 | w | | |
| | | 880 | w | 880 | m |
| | | | | 870 | s |
| | | | | 850 | w |
| | | 725 | vs | | |
| | | 666 | m | | |

## Discussion

It is suggested that the mechanism of the interaction of gamma radiation with the allyl halides involves an initiation stage similar to that already outlined for the radiolysis of alkyl halides, namely, homolytic splitting of the carbon-halogen bond. However, as the allyl halides are unsaturated compounds, the double bond will more readily facilitate the occurrence of chain reactions, and the halogen atom, formed by the initiation step, will attack further molecules of the allyl halide to produce other free radicals. At any time, termination may occur by a step involving the combination of any two free radicals. The following mechanism is proposed for allyl bromide.

Initiation.

$$CH_2{=}CH{-}CH_2Br \longrightarrow CH_2{=}CH{-}\dot{C}H_2 + Br^{\cdot} \qquad \ldots(1)$$

Propagation

$$CH_2{=}CH{-}CH_2Br + Br^{\cdot} \longrightarrow BrCH_2{-}\dot{C}H{-}CH_2Br \qquad \ldots(2)$$

$$CH_2{=}CH{-}CH_2Br + BrCH_2{-}\dot{C}H{-}CH_2Br \longrightarrow \begin{matrix} BrCH_2{-}CH{-}CH_2Br \\ | \\ CH_2{-}\dot{C}H{-}CH_2Br \end{matrix} \qquad \ldots(3)$$

$$CH_2{=}CH{-}CH_2Br + \begin{matrix} BrCH_2{-}CH{-}CH_2Br \\ | \\ CH_2{-}\dot{C}H{-}CH_2Br \end{matrix} \longrightarrow BrCH_2{-}\overset{CH_2Br}{\overset{|}{C}}H{-}CH_2{-}\overset{CH_2Br}{\overset{|}{C}}H{-}CH_2{-}\dot{C}H{-}CH_2Br \qquad \ldots(4)$$

Radical Rearrangement.

$$BrCH_2-\underset{\displaystyle CH_2-\dot{C}H-CH_2Br}{\overset{}{CH}}-CH_2Br \longrightarrow BrCH_2-\underset{\displaystyle CH_2-CHBr-\dot{C}H_2}{\overset{}{CH}}-CH_2Br \quad \ldots(5)$$

Termination

$$BrCH_2-\overset{CH_2Br}{\overset{|}{CH}}-CH_2-\dot{C}H-CH_2Br \longrightarrow BrCH_2-\overset{CH_2Br}{\overset{|}{CH}}-CH_2-CH=CH_2 + Br^{\cdot} \quad \ldots(6)$$

$$BrCH_2-\overset{CH_2Br}{\overset{|}{CH}}-CH_2-CHBr-\dot{C}H_2 \longrightarrow BrCH_2-\overset{CH_2Br}{\overset{|}{CH}}-CH_2-CH=CH_2 + Br^{\cdot} \quad \ldots(6a)$$

$$BrCH_2-\overset{CH_2Br}{\overset{|}{CH}}-CH_2-\dot{C}H-CH_2Br + CH_2=CH-CH_2Br \longrightarrow BrCH_2-\overset{CH_2Br}{\overset{|}{CH}}-CH_2-CH=CH_2 + BrCH_2-\dot{C}H-CH_2Br \quad \ldots(7)$$

$$BrCH_2-\overset{CH_2Br}{\overset{|}{CH}}-CH_2-CHBr-\dot{C}H_2 + CH_2=CH-CH_2Br \longrightarrow BrCH_2-\overset{CH_2Br}{\overset{|}{CH}}-CH_2-CH=CH_2 + BrCH_2-\dot{C}H-CH_2Br \quad \ldots(7a)$$

$$BrCH_2-\overset{CH_2Br}{\overset{|}{CH}}-CH_2-\overset{CH_2Br}{\overset{|}{CH}}-CH_2-\dot{C}H-CH_2Br \longrightarrow BrCH_2-\overset{CH_2Br}{\overset{|}{CH}}-CH_2-\overset{CH_2Br}{\overset{|}{CH}}-CH_2-CH=CH_2 + Br^{\cdot} \quad \ldots(8)$$

$$CH_2=CH-CH_2Br + BrCH_2-\dot{C}H-CH_2Br \longrightarrow CH_2=CH-\dot{C}HBr + BrCH_2-CH_2-CH_2Br \quad \ldots(9)$$

$$CH_2=CH-\dot{C}HBr \leftrightarrow \dot{C}H_2-CH=CHBr$$

$$CH_2=CH-CH_2Br + CH_2=CH-\dot{C}H_2 \longrightarrow CH_2=CH-\dot{C}HBr + CH_2=CH-CH_3 \quad \ldots(10)$$

$$CH_2=CH-CH_2Br + BrCH_2-\underset{\displaystyle CH_2Br}{\overset{|}{C}}H-CH_2-CHBr-\dot{C}H_2 \longrightarrow CH_2=CH-\dot{C}HBr + BrCH_2-\underset{\displaystyle CH_2Br}{\overset{|}{C}}H-CH_2-CHBr-CH_3 \quad ...(11)$$

$$CH_2=CH-\dot{C}H_2 + CH_2=CH-\dot{C}H_2 \longrightarrow CH_2=CHCH_2CH_2CH=CH_2 \quad ...(12)$$

$$BrCH_2-\dot{C}H-CH_2Br + Br^{\bullet} \longrightarrow BrCH_2-CHBr-CH_2Br \quad ...(13)$$

$$\dot{C}H_2CH=CHBr + Br^{\bullet} \longrightarrow BrCH_2CH=CHBr \quad ...(14)$$

Such a reaction mechanism accounts for all the observed reaction products from the irradiation of allyl bromide.

The homolytic splitting of the carbon-halogen bond (Reaction step 1) in the initiation stage during the radiolysis of alkyl halides and halogenated alkenes is now well established,[28,32,33] whether by the direct preferential absorption of energy at that bond or by intramolecular energy transfer which localises the absorbed energy at that site. The formation of no ethylene, substituted ethylenes, or methyl bromide confirms that no carbon-carbon bond splitting occurs in the radiolysis of allyl bromide.

The formation of the dibromo isopropyl radical (Reaction 2) is a vital stage in the scheme as this radical is obviously the precursor of most of the brominated substances isolated from the irradiation.

Most of the reaction scheme proposed follows the

accepted pattern of free radical mechanisms, reaction 5, however, is of greater interest. This type of rearrangement, although rare, is not without precedent. Walling[77] has reviewed a number of reactions, including the free radical addition of trichlorobromomethane to 3,3,3-trichloropropene, in which the migration of a chlorine atom to the β-position in a chlorinated propyl radical has been postulated. Recently, the gamma radiation-induced isomerisation of n-propyl chloride has been reported[78] and the crucial part of the proposed reaction scheme is, also, the migration of the chlorine atom in the chloroisopropyl radical to the β-carbon atom.

$$CH_2\dot{C}HCH_2Cl \longrightarrow CH_3CHCl\dot{C}H_2$$

The dimer of allyl bromide may be formed from either the rearranged or non-rearranged dimer radical by disproportionation (Reactions (6) and (6a)) or by interactions of these radicals with molecules of allyl bromide (Reactions (7) and (7a)). If, however, the trimer molecule has a similar structure to that proposed by Staudinger and Fleitmann[60] for polyallyl chloride, the trimeric radical, which would also be able to undergo rearrangement, could only be produced from the non-rearranged dimer radical (Reaction (4)). That such rearrangement of the dimeric radical takes place is confirmed by the production of 1,4-dibromo-2-bromomethylpentane (Reaction (11)).

The formation of the latter compound, 1,3-dibromopropane and propylene, must result from α-hydrogen abstraction from

allyl bromide molecules by the appropriate radicals (Reaction (11), (12),(13)). The formation of propylene is unusual, as allyl radicals are normally found to dimerise, giving diallyl, or to react more readily with other radicals rather than to abstract hydrogen[79]. As the allyl radicals, however, are formed during the initiation stage, they may be more energetic than those previously investigated and so be capable of such abstractions.

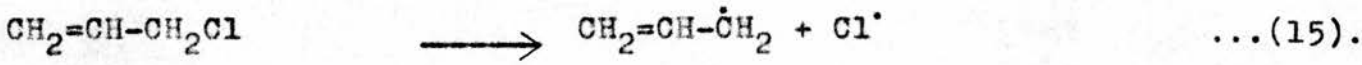
Such hydrogen abstraction would also lead to the formation of bromo-allyl radicals:-

$$CH_2=CH-\dot{C}HBr \longleftrightarrow \dot{C}H_2-CH=CHBr$$

which would explain the formation of the 1,3-dibromoprop-1-enes on reaction with a bromine atom (Reaction (14)). It is of interest to note that the total yield of the isomeric 1,3-dibromoprop-1-enes was much larger than that of 1,3-dibromopropane, propylene, or 1,4-dibromo-2-bromomethyl-pentane, each of whose formation would result in the additional formation of the dibromopropenes. The formation of such halogen substituted allyl radicals has been proposed previously to explain certain results in the benzoyl peroxide catalysed polymerisation of allyl chloride[80].

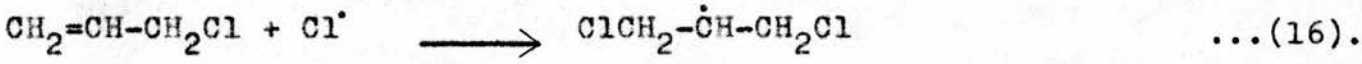
The radiolysis of allyl chloride is assumed to follow the same initial course as the allyl bromide, although the subsequent propagation and termination reactions follow a more definite single route (i.e. polymer formation).

Initiation.

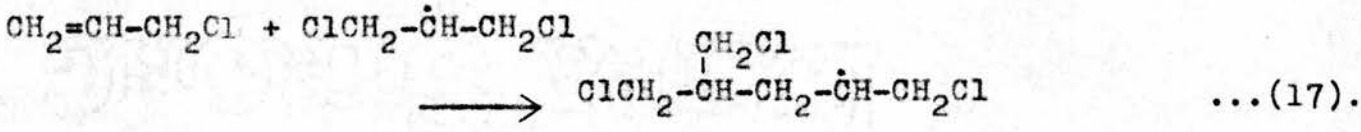


...(15).

Propagation.



...(16).



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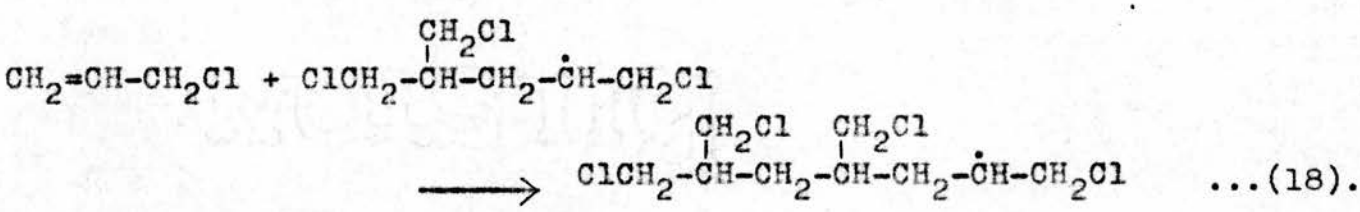

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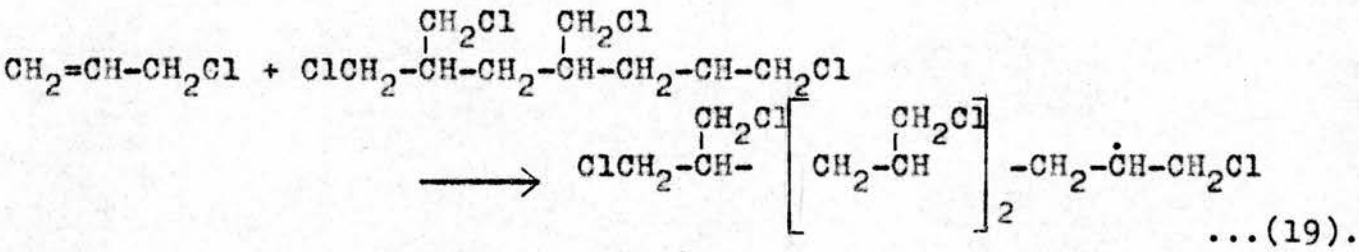
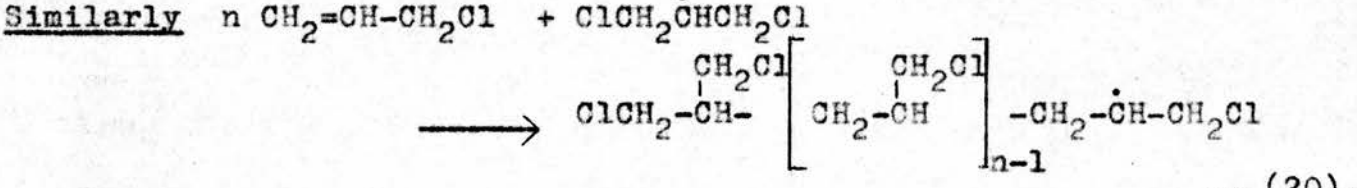


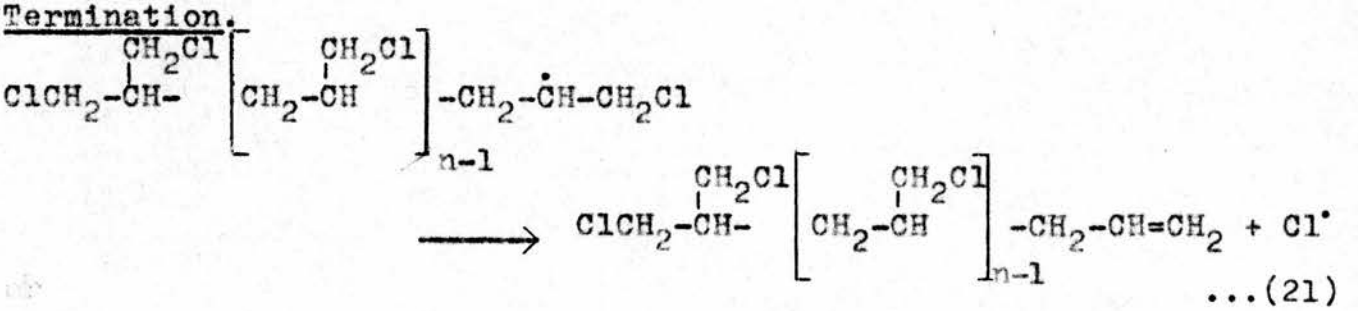
...(19).

Similarly



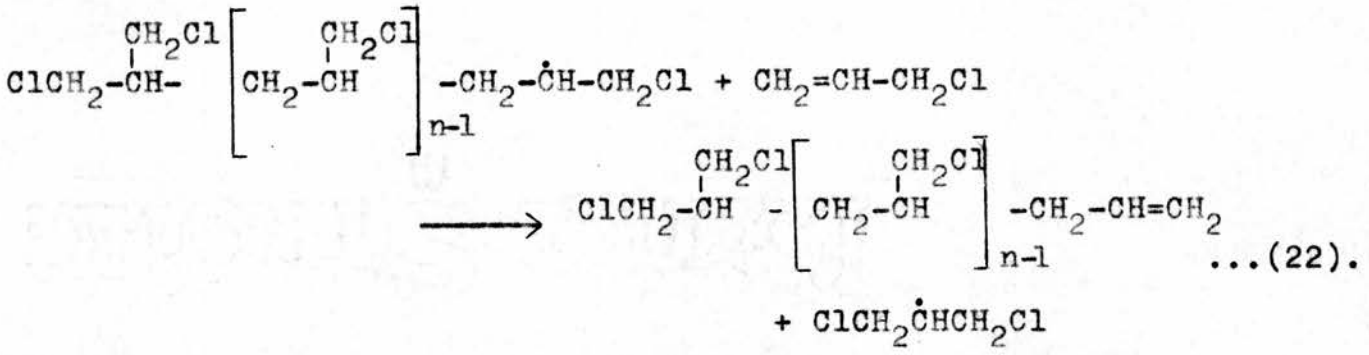
...(20).

Termination.



...(21)

or



$$ClCH_2\text{-}\underset{\displaystyle CH_2Cl}{\underset{|}{CH}}\text{-} \left[ CH_2\text{-}\underset{\displaystyle CH_2Cl}{\underset{|}{CH}} \right]_{n-1} \text{-}CH_2\text{-}\dot{C}H\text{-}CH_2Cl + CH_2{=}CH\text{-}CH_2Cl$$

$$\longrightarrow ClCH_2\text{-}\underset{\displaystyle CH_2Cl}{\underset{|}{CH}} - \left[ CH_2\text{-}\underset{\displaystyle CH_2Cl}{\underset{|}{CH}} \right]_{n-1} \text{-}CH_2\text{-}CH{=}CH_2 \qquad \ldots(22).$$

$$+ ClCH_2\dot{C}HCH_2Cl$$

The formation of only low molecular weight polymeric products from both allyl systems arises because termination of the growing radical chain occurs by the ready elimination of a halogen atom from the polymeric radical (Reactions (6), (7), (21)). The more ready loss of a bromine atom than of a chlorine atom and the consequent greater ease of termination when bromine is involved is the reason for the formation of dimer, and a small amount of trimer, as the only polymeric products from the radiolysis of allyl bromide. This type of termination reaction may also be used to explain the temperature dependence of dimeric yields in the peroxide catalysed polymerisation of allyl chloride where the easier loss of a chlorine atom at higher temperature leads to greater yields of dimer[81].

The smaller degree of total conversion of allyl bromide during radiolysis, ($G_{-C_3H_5Br} = 137$, $G_{-C_3H_5Cl} = 369$), although C-Br bond rupture will take place more readily than C-Cl bond splitting, must be due to the fact that the chain carriers in allyl bromide are dissipated by alternative reactions giving a larger variety of products.

The lack of formation of detectable amounts of propylene or diallyl from the irradiation of allyl chloride indicates that the allyl radicals produced in the initiation stage must be removed by some other mechanism. This may result from recombination of allyl radicals with halogen (chlorine) atoms which are not removed by other reactions as is the case for allyl bromide.

The failure of allyl iodide to polymerise on irradiation probably arises because the initially produced iodine atoms will readily combine to produce iodine molecules which act as efficient radical scavengers[1,82]. The allyl radicals in this system will attack the free iodine to produce allyl iodide and liberate a further iodine atom,

$$CH_2{=}CH{-}\dot{C}H_2 + I_2 \longrightarrow CH_2{=}CH{-}CH_2I + I^{\cdot}$$

which would explain why only a very small amount of diallyl is formed.

## SECTION II.

## The Irradiation of trans-1,2-dichloroethylene.

During the past thirty years, many attempts have been made to polymerise the symmetrical dichloroethylenes, and have shown that no high polymers, comparable with those obtained from vinyl compounds or unsymmetrical dichloroethylene, are formed in quantity. Small amounts of solid have been reported from the photochemically induced reaction of the trans isomer[83], and Mahncke and Noyes obtained a little solid from the vapours of both isomers, using ultra-violet light[84].

Various patent specifications describe the liquid phase polymerisation of both isomers with peroxide catalysts or in ultra-violet light, the products obtained being almost entirely liquid polymers, with total yields up to 35% and a weight ratio of dimer to higher polymers varying from 0.5 to 3.5 at higher temperatures[85]. Bauer, for example obtained 16.6% dimer, 13.5% of higher liquid polymers and also 1.5% of insoluble solid polymer by prolonged heating under reflux (200 hours) of the trans isomer with 1% by weight of benzoyl peroxide[86].

The effect of temperature on this polymerisation has been studied by Franck and Blackham[81] who noted increasing dimerisation at higher temperatures with a dimer:higher polymer ratio of 1:1 at 70°C. Weale has also studied the effect of temperature as well as pressure on the catalysed polymerisation of trans-dichloroethylene and the total yield was found to increase markedly with temperature and, to a small extent, with pressure[87]. High pressures, however, tend to decrease and

higher temperatures to increase the ratio of dimer to higher polymers. The effect of pressure on the catalysed polymerisation of the 1,2-dichloroethylenes has also been studied by Ewald and others who confirmed these results[88]. Weale obtained 22% dimer, 50% higher liquid polymer and 10% solid polymer on reacting the trans isomer for 140 hours at 75°C and 3000 atmospheres pressure and, after 70 hours at 75°C and 8,000 atmospheres, 70% of liquid polymers and 20% solid polymer. The insoluble solid isolated by Weale was a white amorphous powder (Cl found 74.6%, Cl calculated for $C_2H_2Cl_2$ 73.1%) which swelled in contact with organic solvents. It was unchanged at 160-170°C, softened slightly at higher temperatures and fumed at 215°C.

Recently, a study of the irradiation of degassed samples of both cis and trans-1,2-dichloroethylene with helium ions, electrons, and $^{60}Co$ gamma rays has been reported by Futrell and Newton.[89] No significant changes are noted in the G values of the volatile products from different radiation sources and this implies the absence of track effects in events leading to the formation of these compounds. There are, however, striking differences in the ratios of polymer products, yields increasing on changing the radiation from helium ions to gamma rays, although the results are consistent with the differences in radical densities produced by these two types of radiation.

It is, however, difficult to interpret the results given by Futrell and Newton as in a Ph.D. thesis published by Futrell,

it is stated that no solid polymer was obtained from the irradiation of pure trans-1,2-dichloroethylene with gamma rays. This contrasts sharply with results obtained in this department, where the yield of solid polymer was approximately 20% of the total polymer. In the more recent publication, however, Futrell and Newton report the formation of considerable solid polymer which precipitates during the irradiation. No description of this polymer is given and the G value quoted for polymer formation, in moles of monomer removed, is 140. No value is given for the formation of solid polymer.

In the gamma ray induced radiolysis of trans-1,2-dichloroethylene at room temperature described by Taylor[39] an approximate G value for total polymer (containing 70% insoluble solid) of 1350 was reported at a dose-rate of approximately 200r/ml/min. From subsequent experience, both this result and the percentage of solid were considered to be too large and an irradiation was carried out under similar conditions to verify this. At a dose-rate of approximately 304r/ml/min, a G value for total polymer of 960 was obtained and a ratio of solid to total polymer of 20.4% found. It is difficult to understand why such a high yield of solid polymer was obtained in the first irradiation although it is stated that the solid was still swollen with some oil polymers and possibly monomer.

Taylor also irradiated trans-1,2-dichloroethylene at -48°C, at which temperature very little polymeric material

was observed, and at 48°C. At the higher temperature, the amount of total polymer was found to be greatly increased, although the percentage of solid polymer was much reduced (10.1%).

A number of irradiations will now be described which were made in order to determine the G value for the production of polymer from trans-1,2-dichloroethylene and to determine the amount of solid polymer formed. Studies on the dimer of 1,2-dichloroethylene (1,3,4,4-tetrachlorobut-1-ene) will also be described.

## Experimental.

B.D.H. commercial grade dichloroethylene, which was normally found to contain 70 to 90% of the trans isomer, was purified by fractional distillation until the distillate contained no more than 0.5% of the cis isomer measured by G.L.C. The trans-1,2-dichloroethylene was then dried over calcium chloride, stored in the dark, and quickly distilled before irradiation, $n_D^{20}$ 1.4450 (Lit. $n_D^{20}$ 1.4448).

In each case, for the irradiations whose results are shown in Table 4, 435 mls. of trans-1,2-dichloroethylene were irradiated at a dose-rate of 1390r/ml/min (i.e. $8.093 \times 10^{16}$ eV/ml/min) in a stoppered annular Pyrex glass vessel. When the irradiated solution was removed from the $^{60}Co$ source, the solid polymer, most of which had precipitated during the irradiation, was filtered off and washed three times with ether. The ether washings were then added to the liquid polymers, after removal of the monomer by distillation, and the rest of the solid, which precipitated on the addition of the ether, was filtered off. This solid was then washed with ether and added to the initial solid which was then dried. The ether washings were again added to the liquid polymers and the ether was distilled off. The amounts of liquid polymer and solid polymer were then determined by weighing.

The rate of absorption of energy by the trans-1,2-dichloro-

ethylene during irradiation was calculated thus:-

Dose-rate measured by ferrous sulphate dosimeter $= 8.093 \times 10^{16}$ eV/ml/min

Conversion factor $= \frac{\text{Ne } C_2H_2Cl_2}{\text{Ne ferrous sulphate}}$

Ne $C_2H_2Cl$ $= \frac{1.2569}{96.95} \times N \times 48 = 6.223 \times 10^{-1}$ N.

Ne ferrous sulphate $= 5.682 \times 10^{-1}$ N.

Conversion factor $= \frac{6.223 \times 10^{-1} N}{5.682 \times 10^{-1} N} = 1.095.$

Rate of absorption by dichloroethylene $= 8.093 \times 1.095 \times 10^{16}$ eV/ml/min.

$= 8.863 \times 10^{16}$ eV/ml/min.

From a graph of total polymer formed against total dose absorbed, the G value for the production of polymer is 206. However, from the G values in Table 4, it is seen that the G value for total polymer decreases with increasing dose, and by extrapolating a graph, of G value against total dose, to zero a value of 225 is obtained. This latter value is probably more accurate, as any effects, due to removal of monomer during irradiation, are minimised.

In irradiation 2, in which 435 mls of trans dichloroethylene were irradiated for 69½ hours (Table 4), the amounts of dimer and trimer formed were also determined. The weight of dimer ($n_D^{20}$ 1.5140) was 4.6 gms and the weight of trimer ($n_D^{20}$ 1.5380) was 4.2 gms. Those weights were of the crude fractions which

had been separated from the remaining liquid polymers by distillation and no accuracy is claimed for the results, which were determined merely to give some impression of the yield of the liquid polymers at this dose rate.

A large scale irradiation of trans-dichloroethylene was also carried out in order to check the results obtained by Taylor. Trans-dichloroethylene (1114 mls containing 10% cis-isomer) was irradiated for 92 hours at a dose-rate of 304r/ml/min. The weight of solid polymer obtained was 36.9 gms and the weight of liquid polymer 144 gms. The G value for the production of the solid polymer was 196 and for total polymer 961. The ratio of solid polymer to total polymer in this case is 20.4%.

Table 4.

Polymer Yields from $\gamma$-radiolysis of Trans-1,2-dichloroethylene.

| Irr. Time hours | Total dose absorbed eV/ml x $10^{-20}$ | Solid Polymer gms | Solid Polymer M, $C_2H_2Cl_2$/ml x $10^4$ | Liquid Polymer gms | Total Polymer gms | Total Polymer M, $C_2H_2Cl_2$/ml x $10^{3.2}$ | Percentage Solid Polymer | G Value Insoluble Polymer | G Value Total Polymer |
|---|---|---|---|---|---|---|---|---|---|
| 45 | 2.393 | 6.87 | 1.629 | 29.7 | 36.6 | 0.868 | 18.8 | 41.0 | 218 |
| 69.5 | 3.697 | 11.02 | 2.614 | 44.4 | 55.4 | 1.314 | 19.9 | 42.6 | 214 |
| 116.5 | 6.197 | 19.6 | 4.648 | 68.7 | 88.3 | 2.094 | 22.1 | 45.1 | 203 |
| 162 | 8.614 | 28.6 | 6.782 | 93.6 | 121.2 | 2.874 | 23.4 | 47.4 | 201 |
| 214 | 11.38 | 39.1 | 9.271 | 118.6 | 157.7 | 3.740 | 24.8 | 49.1 | 198 |

FIGURE 6

TOTAL POLYMER PRODUCTION FROM

TRANS-1,2-DICHLOROETHYLENE

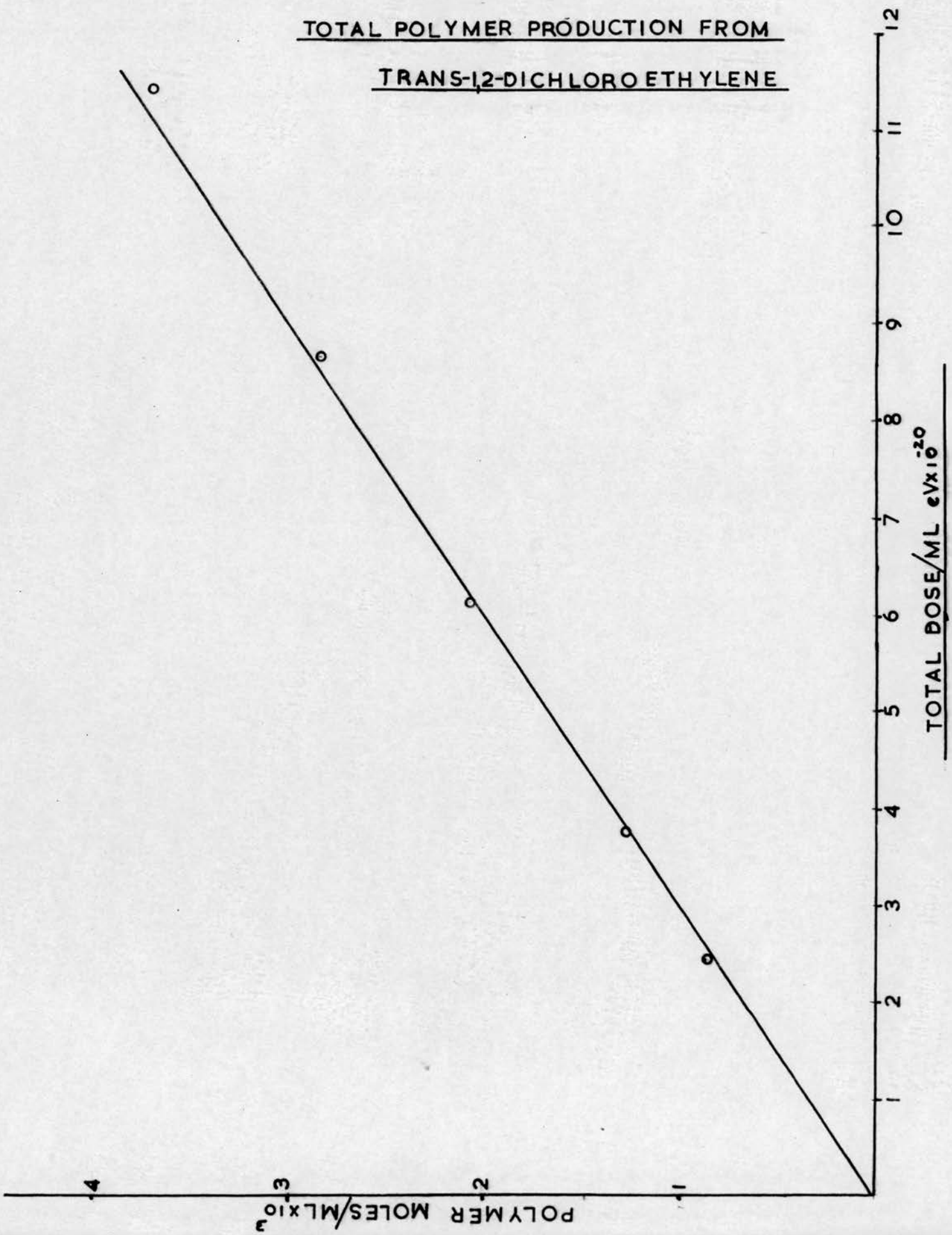


FIGURE 7

G VALUE against TOTAL DOSE

Separation and identification of the isomeric 1,3,4,4-tetrachlorobut-1-enes.

Taylor noted that the physical constants of the dimer fraction obtained from the radiolysis of cis and trans-1,2-dichloroethylene agreed with those quoted by Frank and Blackham for 1,3,4,4-tetrachlorobut-1-ene, produced by the benzoyl peroxide catalysed polymerisation of these compounds[81], i.e. $Cl_2HC-CHCl-CH=CHCl$. The constants are given below.

Dimer formed by trans-1,2-dichloroethylene $n_D^{20}$ 1.5146 $D_4^{20}$ 1.475 b.p. 83-84°C/15mm

Dimer formed by cis-1,2-dichloroethylene $n_D^{20}$ 1.5150 $D_4^{20}$ 1.474 b.p. 83-84°C/15mm

Literature $n_D^{20}$ 1.5150 $D_4^{20}$ 1.473 b.p. 88°C/20mm.

This dimer was assumed to be a pure compound and it was stated that no geometrical isomerism could be detected, and that the compound appeared to have a trans-configuration. A close study, however, of the infra spectrum of this dimer also revealed the presence of certain absorptions which were indicative of a cis-configuration at the double bond.

Studies were therefore made of the dimeric mixture in an attempt to separate the isomers by G.L.C. It was found possible to achieve such separation on the analytical unit, using both silicone fluid and T.C.P. as stationary phases. Two major components were detected and no significant difference was found between the dimeric fractions produced by the radiolysis

of cis and trans-dichloroethylene or between these and samples prepared by the benzoyl peroxide catalysed polymerisation of these compounds.

Attempts were then made to separate larger amounts of these compounds using the preparative scale G.L.C. unit employing an 8' column of 25 mm i.d. The first column packing used was silicone elastomer E301 (30% by weight on 40-60 mesh firebrick) but only incomplete resolution of the two components was achieved. A column packing of sodium dodecylbenzenesulphonate ("Tide" washing powder) which had been dried for three days at 130°C was then used, but it was found that this packing caused the tetrachlorobut-1-enes to decompose to give cis and trans-dichloroethylenes. Good separations of 1 ml injections, without decomposition, were, however, obtained using a column packing of 30% T.C.P. on firebrick (40-60 mesh) at 130°C with a gas flow rate of 300 mls/minute of nitrogen. Under these conditions, the first isomer had a retention time of 250 minutes and the second isomer of 310 minutes. After collection, the fractions were distilled in a molecular still to free them from any traces of contaminants from the column and their physical constants were measured.

Fraction 1. $n_D^{20}$ 1.5132 b.p. 193-195°C/760mm.

Fraction 2. $n_D^{20}$ 1.5198 b.p. 197-198°C/760mm.

The boiling points of the two pure fractions were determined by a micro-capillary technique - Siwoloboff's method.

It is of interest to note, at this point, that Futrell and Newton[89] detected the presence of the two 1,3,4,4-tetrachlorobut-1-enes by G.L.C. and from boiling point-emergence time correlations for chlorinated hydrocarbons, estimated a boiling point range of 187-203°C for these compounds.

Chemical analyses were obtained for both samples which indicated the expected empirical formula $C_2H_2Cl_2$.

| Analysis found Fraction 1. | Analysis found Fraction 2. | Analysis calc. for $C_2H_2Cl_2$. |
|---|---|---|
| C = 25.85% | C = 25.84% | C = 24.8% |
| H = 2.01% | H = 2.24% | H = 2.1% |
| Cl = 72.20% | Cl = 71.80% | Cl = 73.1% |
| 100.06 | 99.88 | |

Infra-red spectra for both compounds were then obtained (Page 72). Fraction 1 showed strong absorptions at 1636cm$^{-1}$ and 1239cm$^{-1}$ as well as those for C-Cl bonds in the 700-800cm$^{-1}$ region. Fraction 2 gave strong absorptions at 1630cm$^{-1}$ and 936cm$^{-1}$ as well as those for C-Cl. The strong absorption at 936cm$^{-1}$ in Fraction 2 is indicative of a trans-disubstituted compound. Sheppard and Sutherland[90] have used the CH deformation frequency at 965cm$^{-1}$ to establish the configuration about disubstituted ethylenic bonds and Haszeldine[91] reports that direct substitution of a halogen onto the double bond reduces the CH deformation frequency for -CH=CHBr and -CH=CHCl to 935cm$^{-1}$ as has been confirmed by Kitson[92]. The presence of a strong absorption at 1293cm$^{-1}$ in Fraction 1 may be taken as

indicative of a cis disubstituted double bond. Bellamy[93] reports that such a strong absorption would be expected in the infra-red for cis- compounds. The strengths of the C=C stretching vibration absorptions also indicate the presence of a cis configuration in Fraction 1, as the intensity is much stronger for this fraction than for Fraction 2. Trans disubstituted compounds are known to give much weaker absorptions for the C=C stretching vibration than cis, due to the greater degree of symmetry possible in the former type of compound. This classification of the configuration of the two isomers is also in agreement with their boiling points (cf. cis and trans-1,3-dibromoprop-1-ene, Cis b.p. 154-156°C/760mm, Trans b.p. 160°C/760mm)[80].

The stabilities of these two isomers must be about equal as, on standing, isomerisation occurred, a similar mixture being formed in each case. It was also found that, during bromination, the isomerisation rate was greatly increased, a mixture being produced in a few minutes. This was not unexpected as halogens are known to cause the rapid interconversion of geometrical isomers where the stabilities are similar. Bromine initiated isomerisation has been noted by Olson[94] to produce trans-dibromoethylene from the cis-isomer.

Bromination of the 1,3,4,4-tetrachlorobut-1-enes was found to produce two products, one of which was the solid identified by Taylor as 1,2-dibromo-1,3,4,4-tetrachlorobutane,

m.p. 102-103°C.

After removal of the solid from the mixture by filtration, the liquid was distilled (b.p. 70°C/0.05mm $n_D^{20}$ 1.5740) and chemical analyses of both solid and liquid products were obtained.

| Analysis found. Liquid. | Analysis found. Solid. | Analysis calc. for $C_4H_4Cl_4Br_2$ |
|---|---|---|
| C = 14.12% | C = 14.1% | C = 13.6% |
| H = 0.83% | H = 1.3% | H = 1.1% |
| Hal = 85.05% | Hal = 84.7% | Hal = 85.3% |
| 100.0 | 100.1 | |

The two products must, therefore, be stereoisomers. The dimer itself possesses one asymmetric centre and bromination will introduce two more. Infra-red spectra of both bromo-compounds were obtained but no interpretation was possible.

A similar study of the trimer of dichloroethylene was attempted. Only partial separation could be obtained, using 3' columns of 30% silicone elastomer E301 on firebrick under analytical conditions. Four components of this fraction were, however, noted. No application was possible on a preparative scale column, due to the very high boiling point of this fraction ( 300°C) which caused the retention times, even on 18" columns at 130°C, to be excessive.

Infra-red Spectra of cis- and trans-

1,3,4,4-tetrachlorobut-1-ene.

| cis | | trans | |
|---|---|---|---|
| $n_D^{20}$ 1.5132 b.p. 193-195°C | | $n_D^{20}$ 1.5198 b.p. 197-198°C | |
| 3105 | w | | |
| 3070 | w | 3085 | w |
| 3000 | w | 3010 | w |
| | | 1753 | w |
| 1636 | vs | 1630 | s |
| 1350 | w | 1330 | w |
| 1315 | w | | |
| 1293 | vs | 1292 | w |
| 1281 | w | | |
| 1275 | w | | |
| | | 1230 | w |
| 1207 | m | 1207 | w |
| 1188 | m | 1187 | w |
| | | 1118 | w |
| 1095 | m | | |
| 1005 | w | 1007 | w |
| 982 | w | 979 | w |
| 955 | w | 955 | w |
| 932 | w | 936 | vs |
| | | 855 | m |
| 817 | m | 815 | m |

## Discussion.

The primary act in the radiolysis of trans-1,2-dichloroethylene is suggested to involve an initiation stage similar to that already described for the radiolysis of the allyl halides, namely, the homolytic splitting of a carbon-halogen bond. This is also consistent with the conclusion, of Mahnke and Noyes[84], that the primary act of photolysis of the symmetrical dichloroethylenes is the breaking of a C-Cl bond. The chlorine radicals formed by this initiation may then add to a molecule of monomer forming a radical which, on adding a further molecule of dichloroethylene, gives a dimeric radical and eventually, by a series of such additions, a polymeric radical as is the case for allyl chloride, i.e.

Initiation.

$$CHCl{=}CHCl \longrightarrow CHCl{=}\dot{C}H + Cl^{\cdot} \qquad ...(1)$$

Propagation.

$$CHCl{=}CHCl + \dot{C}l \longrightarrow CHCl_2\text{-}\dot{C}HCl \qquad ...(2)$$

$$CHCl{=}CHCl + CHCl_2\text{-}\dot{C}HCl \longrightarrow CHCl_2\text{-}CHCl\text{-}CHCl\text{-}\dot{C}HCl \qquad ...(3)$$

$$CHCl{=}CHCl + CHCl_2\text{-}CHCl\text{-}CHCl\text{-}\dot{C}HCl \longrightarrow CHCl_2\text{-}\left[CHCl\right]_n\text{-}\dot{C}HCl \qquad ...(4)$$

where n = 0, 2, 4, etc..

Termination.

$$CHCl_2\text{-}CHCl\text{-}CHCl\text{-}\dot{C}HCl \longrightarrow CHCl_2\text{-}CHCl\text{-}CH{=}CHCl + \dot{C}l \quad ...(5)$$

$$CHCl_2\text{-}\left[CHCl\right]_{n-1}\text{-}CHCl\text{-}\dot{C}HCl \longrightarrow CHCl_2\text{-}\left[CHCl\right]_{n-1}\text{-}CH{=}CHCl + \dot{C}l \quad ...(6)$$

or

$$CHCl_2\text{-}\left[CHCl\right]_{n-1}\text{-}CHCl\text{-}\dot{C}HCl + CHCl{=}CHCl \longrightarrow CHCl_2\text{-}\left[CHCl\right]_{n-1}\text{-}CH{=}CHCl + CHCl_2\text{-}\dot{C}HCl \quad ...(7)$$

Although this radical scheme explains the formation of the polymeric products observed from the irradiation of trans-1,2-dichloroethylene, other reactions of the intermediate radicals are possible. Some additional reactions have been described by Futrell and Newton[89] to explain a number of other products and the isomerisation effect which they noted. These other products were not detected by Taylor and, as the purpose of the present investigation was to determine quantitatively only the polymer yields, they will not be discussed at length.

It is of interest to note, however, that Futrell and Newton detected the formation of 1,1,2,2-tetrachlorethane and 1,2,3,4,4-pentachlorobut-1-ene and stated that the yield of these products decreased significantly on changing the irradiation source from helium ions to gamma rays. Their formation was believed to be a result of the following reactions:-

$$CHCl_2\text{-}\dot{C}HCl + Cl^{\cdot} \longrightarrow CHCl_2\text{-}CHCl_2$$

and

$$C_2H_2Cl_2 \longrightarrow CHCl{=}CCl^{\cdot} + \dot{H}$$

$$CHCl{=}CCl^{\cdot} + CHCl_2\text{-}\dot{C}HCl \longrightarrow CHCl_2\text{-}CHCl\text{-}CCl{=}CHCl$$

The lower yield in the gamma ray radiolysis is due to the decrease in radical density as the secondary electron produced leaves a long sparsely ionised track where the possibility of radical recombination is reduced. The greater degree of such recombinations in the expanding helium ion tracks also decreases the total polymer yields significantly.

The effect of dose-rate on polymer yields in the gamma ray irradiations of trans-1,2-dichloroethylene is also of interest. Futrell and Newton noted a G value, for total polymer, of 140 at a dose-rate of $1.56 \times 10^{18}$ eV/ml/min and the G value found in the present work was 225 at a dose-rate of $8.863 \times 10^{16}$ eV/ml/min. This is because, if the dose-rate is very small, the reactive fragments, i.e. radicals, will be formed along a few isolated columns and they will be able to diffuse to other parts of the system where they will be able to react with stable molecules to give rise to polymeric radicals. As the dose-rate is increased, however, the concentration of radicals will become greater and reach a stage where the medium is effectively homogeneous with respect to them, and their ability to diffuse will be of little significance. These conditions favour primary recombination of the radicals to form the initial

species and the total product yields fall. Normally a linear relationship exists between the G value and the square-root of the dose-rate in a homogeneous system. This, obviously, does not apply in the case of the irradiation of trans dichloroethylene, where deposition of solid polymer during the irradiation will upset any normal kinetic interpretation.

The results of the large scale irradiation must be viewed with some caution as the dose-rate quoted is merely the average dose-rate per ml. for the large volume involved. The diameter of this irradiation vessel is large and the flux of radiation from the central rod source will fall off considerably across the vessel. The flux itself decreases inversely as the square of the distance from the source and there will also be a loss of radiation due to interaction with the medium. The dose-rate measured was, therefore, really the mean of widely differing dose-rates at various points in the vessel. As the G value is affected by the dose-rate, this irradiation does not compare with the series performed in the smaller vessels where this element of uncertainty has been reduced.

The effect of the total dose absorbed on the yield of polymer is also of interest. From the results given in Table 4, it may be seen that the G value decreases with increasing total dose, due to the large percentage conversion of the dichloroethylene

obtained. Because of this effect, the initial rate of formation of the polymer had to be determined by extrapolating the radiolytic yields as a function of energy input to zero dose as in Fig 7 .

## SECTION III

## The Irradiation of Tetrachloroethylene.

## Introduction

Previous attempts to polymerise tetrachloroethylene have been largely unsuccessful. Conikberg and Zhulin[95] found no evidence of polymerisation on heating tetrachloroethylene in a steel bomb at 300°C for 56 hours, although a 56% yield of hexachloroethane and hexachlorobuta-1,3-diene was obtained.

Miller irradiated pure tetrachloroethylene with $^{60}Co$ gamma rays and obtained the following products as well as HCl and phosgene.

1) Hexachloroethane.
2) Hexachlorobuta-1,3-diene.
3) A cyclic compound ($C_6Cl_8$) suggested to be octachlorocyclohexa-1,3-diene.
4) Octachloro-but-1-ene.

The calculated G value for the conversion of tetrachloroethylene molecules into product was 9.

No confirmation of the structure of product 3 was given and its structure had been assigned on comparison with literature constants of the isomeric octachlorocyclohexa-1,4-diene. A dienic structure was indicated, however, from the infra-red absorptions at 1641 and 1606$cm^{-1}$. In an aliphatic compound of comparable degree of halogen substitution, e.g. hexachlorobuta-1,3-diene, however, these absorptions would appear at a much lower frequency and the large frequency shift was interpreted on the

basis of a ring structure. An attempt to prepare the isomeric octachlorocyclohexa-1,4-diene had been unsuccessful.

Accordingly, further irradiations of tetrachloroethylene were carried out in order to obtain a specimen of the $C_6Cl_8$ compound for comparison with octachlorocyclohexa-1,4-diene synthesised, in this department, by reaction of tetrachloro-p-benzoquinone with phosphorus pentachloride (Barral[96]).

## Experimental

### Irradiation of Tetrachloroethylene.

Technical grade tetrachloroethylene from Hopkin and Williams was shaken several times with dilute acid , to remove the basic compound present as a stabiliser, washed several times with water and dried with phosphorus pentoxide. It was distilled immediately before use under reduced pressure using a short Vigreux fractionating column (b.p. 40°C/15mm). The tetrachloroethylene used for this irradiation contained not more than 0.5% ethylene dichloride as impurity.

526 mls of the purified tetrachloroethylene were irradiated at a dose-rate of approximately 500r/ml/min for 457 hours.

After the HCl, phosgene, and unchanged tetrachloroethylene had been removed by distillation under reduced pressure (15 mm), hexachloroethane and hexachlorobuta-1,3-diene were removed at a pressure of 0.5 mm. After removal of most of the latter compound, the radiation products were transferred to a vacuum sublimation apparatus, and heated to 100°C at 0.01 mm. Under these conditions, a white crystalline sublimate was obtained on the cold finger (contaminated with hexachlorobuta-1,3-diene). This solid was removed and recrystallised from ethanol to give prisms with a strong camphor-like odour, m.p. 182-183°C. Although the melting point for this product was 20° higher than that quoted

by Miller, the infra-red spectra of the two solids were identical. The compound dissolved in cyclohexane and had a strong absorption in the ultra-violet, giving a broad maximum at 224-226 mμ and e = 22,000 (Log $e_{224}$ = 4.35).

A chemical analysis of this compound confirmed the empirical formula, $C_6Cl_8$.

| Analysis found | Analysis calculated for $C_6Cl_8$ |
|---|---|
| C = 20.1% | C = 20.2% |
| H = 0.2% | |
| Cl = 79.6% | Cl = 79.8% |
| 99.9 | |

Identification of the Compound, $C_6Cl_8$

The irradiation product was compared with octachlorocyclohexa-1,4-diene which had been prepared by the action of $PCl_5$ on p-chloranil at 135-140°C. This compound gave a chemical analysis of 20.66% and 78.65% Cl, had a melting point of 160-161°C and showed only one C=C stretching vibration at 1612$cm^{-1}$ in the infra-red, and was quite dissimilar to the radiation product.

A synthesis of octachlorocyclohexa-1,3-diene was also attempted, using o-chloranil but hexachlorobenzene was the only product obtained. The physical constants of the radiation products agreed with those reported[97] for 1,2,3,3,5,5-hexachloro-4-

dichloromethylene-cyclopentene, a specimen of which was prepared by the following method.[98] Hexachloropropene (prepared by the action of ethanolic KOH on heptachloropropane[99]) was treated with copper bronze in methanol and the resultant red solution was washed with water, extracted with ether, which was then removed, and finally purified by dissolving it in 40-60° petrol ether and passing it through a column of activated alumina using 40-60° petrol ether as the eluant. The solid purified in this way and recrystallised from 80-100° petrol ether had m.p. 182-183°C. No depression of the m.p. was found when this was mixed with the radiation product. An infra-red spectrum of the synthetic product showed absorptions at 1645 and 1605cm$^{-1}$, and was identical with that of the radiation product. This synthetic product also had a strong absorption in the ultra-violet at 224-226 mu. (Log $e_{224}$ = 4.31).

## Infra-Red Spectra of

## 1,2,3,3,5,5-hexachloro-4-dichloromethylene-cyclopentene.

| Radiation Product | Synthesised from hexachloropropene |
|---|---|
| 2360 w | 2340 w |
| 1645 m | 1645 m |
| 1605 w | 1605 w |
| 1208 m | 1210 m |
| 1167 m | 1171 m |
| 942 w | 947 w |
| 930 m | 935 m |
| 805 m | 805 m |

## Discussion.

The radiolysis of tetrachloroethylene is suggested to follow a series of reactions, similar to those already described for the allyl halides and trans-1,2-dichloroethylene, initiated by the splitting of a C-Cl bond as indicated below.

Initation.

$$CCl_2{=}CCl_2 \longrightarrow CCl_2{=}\dot{C}Cl + \dot{C}l \qquad ...(1)$$

Propagation.

$$CCl_2{=}CCl_2 + \dot{C}l \longrightarrow \dot{C}l_2{-}CCl_3 \qquad ...(2)$$

$$CCl_2{=}CCl_2 + \dot{C}Cl_2{-}CCl_3 \longrightarrow \dot{C}Cl_2{-}CCl_2{-}CCl_2{-}CCl_3 \qquad ...(3)$$

$$CCl_2{=}CCl_2 + {}^{\bullet}CCl_2{-}\,CCl_2\,{}_n{-}CCl_3 \longrightarrow {}^{\bullet}Cl_2{-}\,CCl_2\,{-}CCl_3 \quad (n+2) \qquad ...(4)$$

Termination.

$$\dot{C}Cl_2{-}CCl_2{-}CCl_2{-}CCl_3 \longrightarrow CCl_2{=}CCl{-}CCl_2{-}CCl_3 + \dot{C}l \qquad ...(5)$$

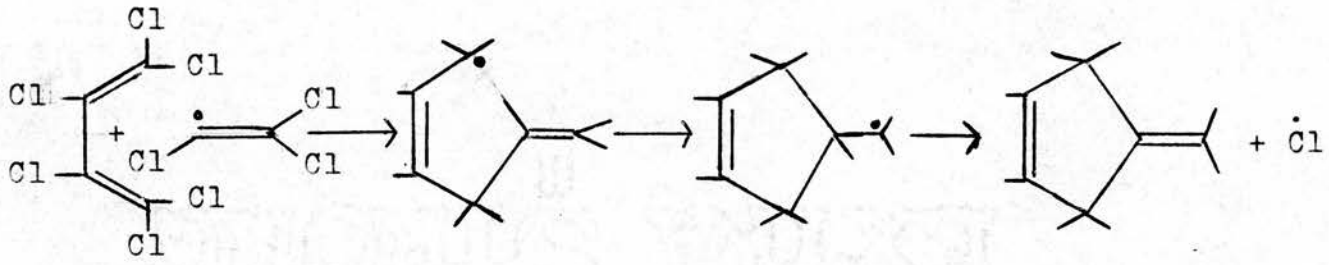
$$CCl_2{=}\dot{C}Cl + \dot{C}Cl_2{-}CCl_3 \longrightarrow CCl_2{=}CCl{-}CCl_2{-}CCl_3 \qquad ...(5a)$$

$$2CCl_2{=}\dot{C}Cl \longrightarrow CCl_2{=}CCl{-}CCl{=}CCl_2 \qquad ...(6)$$

$${}^{\bullet}CCl_2{-}CCl_3 + Cl^{\bullet} \longrightarrow CCl_3{-}CCl_3 \qquad ...(7)$$

Such a reaction mechanism accounts for all the observed

products from the irradiation of tetrachloroethylene, except the 1,2,3,3,5,5-hexachloro-4-dichloromethylene-cyclopentene. The following reactions, involving hexachlorobuta-1,3-diene molecules are suggested to account for its formation.

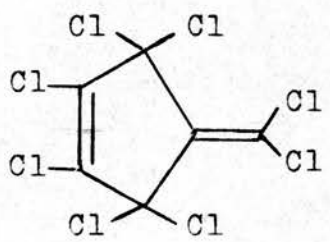


or

$CCl_2=CCl-CCl=CCl_2 \longrightarrow CCl_2=CCl-CCl=\dot{C}Cl + \dot{C}l$

$CCl_2=CCl-CCl=\dot{C}Cl + Cl\dot{C}=CCl_2$

$\longrightarrow CCl_2=CCl-CCl=CCl-CCl=CCl_2$



The latter route involves the attack of the radiation on a hexachlorobuta-1,3-diene molecule to give a radical which would be capable of adding to a trichlorovinyl radical to form octachlorohexatriene. This compound has been shown[97] to

isomerise to the cyclic compound on heating and is an intermediate in its formation by the dechlorination of hexachloropropene. However, since only a small amount of hexachlorobuta-1,3-diene is formed in the irradiation, and Miller had found that the irradiation of this compound resulted in only a very small amount of conversion, the possibility of such radical combinations must be very small.

The first route, involving an attack of the initially formed trichlorovinyl radical from the tetrachloroethylene on a molecule of hexachlorobuta-1,3-diene would, therefore, seem to be the more important one for the formation of the 1,2,3,3,5,5-hexachloro-4-dichloromethylene-cyclopentene.

## General Summary and Discussion.

Cobalt-60 has been used as a source of gamma radiation and the induced chemical effects on various unsaturated organic compounds have been studied.

Preparative scale Gas Liquid Chromatographic techniques have been developed and used in the identification of the irradiation products and analytical G.L.C. has been used for their quantitative determination. For these irradiations, starting materials of high purity were necessary, as free radical reactions are very sensitive to small amounts of impurities, and this was ensured by G.L.C. Infra-red spectrum determinations, which were obtained using a Hilger H800 double beam spectrophotometer or a Perkin-Elmer Infracord spectrophotometer, were used, whenever possible, to confirm the identifications suggested by G.L.C. studies.

The yields of the products obtained from the irradiations have been determined and expressed as G values which represent the number of molecules of product formed or starting material converted to product per 100 eV of energy absorbed. From the ultimate products isolated from these irradiations, the nature of the primary interactions and the ensuing reactions of the initially formed species have been inferred. The results for each of the systems studied are consistent with reaction mechanisms involving homolysis of a carbon-halogen bond as the primary act.

In the irradiation of allyl chloride, allyl bromide, and trans-1,2-dichloroethylene, the initially formed halogen radicals attack molecules of the parent compound acting as the initiators of chain reactions which lead to the formation of high yields of polymeric materials ($G_{-C_2H_2Cl_2} = 225$, $G_{-C_3H_5Cl} = 369$, $G_{-C_3H_5Br} = 137$). The smaller degree of total conversion to polymer of allyl bromide has been explained in terms of the dissipation of the chain carrying radicals by alternative reactions which lead to a much larger number of products (twelve have been detected) than in the irradiation of allyl chloride where polymerisation appears to be the only reaction.

The different degree of polymerisation noted in these irradiations has been shown to depend on the relative stabilities of the polymeric radicals formed and the ease with which they are able to eliminate a halogen atom; an effect which results in a lower degree of polymerisation being obtained from allyl bromide, where mainly dimerisation is noted, than from allyl chloride where degree of polymerisation = 5. The failure to detect any polymerisation from allyl iodide has been explained in terms of the inhibition effect due to the initial formation of iodine which acts as a radical trap.

The formation of 1,4-dibromo-2-bromomethyl-pentane from the radiolysis of allyl bromide has been discussed in terms of a bromine atom transfer in the dimeric radical followed by

hydrogen abstraction. Such hydrogen abstraction reactions are also responsible for the formation of propylene and 1,3-dibromopropane and result in the formation of bromo-allyl radicals which lead to the formation of the 1,3-dibromoprop-1-enes.

The results obtained from the radiolysis of trans-1,2-dichloroethylene have been discussed in terms of total dose absorbed and the rate of energy absorption and compared with those found using helium ions, where the greater radical densities produced alter the distribution of the products obtained.

Studies have also been made on the dimeric fraction obtained from the radiolysis of dichloroethylene and two isomeric 1,3,4,4-tetrachlorobut-1-enes have been isolated by preparative scale G.L.C. and their configurations determined on the basis of their infra-red absorption frequencies.

The major factor contributing to the small amount of conversion of tetrachloroethylene on radiolysis with gamma rays ($G_{-C_2Cl_4} = 9$) is considered to be due to the difficulty of free radical attack on the sterically shielded double bond. A mechanism has been proposed to account for the formation of 1,2,3,3,5,5-hexachloro-4-dichloromethylene-cyclopentene.

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